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A METAL ANALYSIS SURVEY OF 43 CANADIAN COMMERCIAL COALS

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ABSTRACT

A wide spectrum of Canadian commercial coals was analysed in order to establish the metal concentration range of selected major, minor and trace elements of technological concern. Analytical data obtained from the analysis of raw coal by neutron activation procedures was compared with data obtained from pretreated coal analysed by a wide variety of instrumental techniques utilized at ERL. Statistical analysis of the resulting data was employed to verify the instrumental techniques most suitable for each element and to isolate potential sources of analytical error.

The Analysis and Standardization section's analytical techniques are compared to neutron activation analysis on the whole coal dry basis to isolate analytical problems associated with sample pre-treatment and establish procedures to compile and analyse future analytical surveys.

ÉTUDE DES RÉSULTATS D'ANALYSE DES ÉLÉMENTS MÉTALLIQUES DE 43 CHARBONS CANADIENS DE QUALITÉ COMMERCIALE

par

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RÉSUMÉ

On a procédé à l'analyse de toute une gamme de charbons canadiens de qualité commerciale dans le but de déterminer la concentration de métaux contenus dans des éléments majeurs, mineurs et traces choisis ayant un intérêt technique. On a comparé les données d'analyse d'un charbon brut par la méthode d'activation par neutrons aux données obtenues de l'analyse d'un charbon prétraité faite selon les techniques d'analyse variées utilisées à LRE. Les résultats de l'analyse statistique des données de cette comparaison ont été utilisés afin de vérifier les techniques d'analyse qui conviennent le mieux à chaque élément ainsi que de relever les sources d'erreurs possibles lors de l'analyse.

De plus, les techniques d'analyse de la Section de l'analyse et de la normalisation ont été comparées à l'analyse d'un charbon brut à sec par la méthode d'activation par neutrons afin de relever les problèmes d'analyse associés au prétraitement de l'échantillon et de créer une méthode de compilation et d'analyse pour les études analytiques ultérieures.

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INTRODUCTION

43 coal samples were selected from mines across Canada. These samples were subjected to metals analysis by neutron activation analysis (Becquerel Laboratories) and various other routine methods used by the Analysis and Standardization Section, Energy Research Laboratories, CANMET.

Rapid, inexpensive, quantitative determination of elemental concentrations in coal is essential to efficient utilization in industrial processes. The concentrations of mineral constituents in the coal cause it to have varying endothermic, gas producing and scavenging reactions as well as abrasion and slag formation properties. A knowledge of these properties is critical in research and pilot plant testing operations.

Coal analysis has gained impetus as more precisely characterized coal allows far better blending for thermal power generation and facilitates design and maintenance of on site coal upgrading and pollution abatement units. This work thus encourages petroleum feedstock and environment quality conservation.

Coal metal analysis generally comprises techniques such as heating, ashing, fusing and sample digestion or solvation entailing steps prone to matrix degradation, analyte volatilization, and contamination.

Neutron activation analysis is a method based on subjecting an air-dried sample to a neutron flux then measuring the radioactive particle energies indicative of metal concentrations in the sample.

Significant statistics from analysis of a suite of pretreated Canadian commercial coals were used to compare neutron activation with ERL techniques, establish cross procedural precision values and localize method sources of error.

The correlational techniques developed here will be used in further work on method validation.

ANALYTICAL PROCEDURES

Each sample was analyzed for 18 elements by the Analysis and Standardization Section of Energy Research Laboratories using various techniques on both the coal and lithium tetraborate fusions of the ash. They were then analyzed by Becquerel Laboratories using neutron activation analysis for 16 of the same elements, excluding fluorine and phosphorus. Sulphur was listed

as being consistently below its detection limits. Thus 15 elements can be cross-correlated.

An outline of the important features of each analytical method follows:

Na

The sodium analysis is done using a Beckman Spectraspan V directly coupled plasma analyzer after a three-stage sample work-up.

The analyte is slowly heated to 750 C in air and maintained overnight. The ash is agate-ground to pass a 200-mesh sieve, and reashed.

Ash (0.1 g) and $Li_2B_4O_7$ (0.5 g) is then carefully weighed into a platinum crucible, mixed, and swirl-fused at 1050 C in a muffle oven. The glass is then weighed to determine the size of any small loss on fusion.

The glass is then dissolved with 5 vol % analytical grade nitric acid and poured into 0.1 L volumetric flasks.

The directly coupled plasma analyzer is then centered at Na emission line at 589.6 nm and standardized using glass alone zero and 10 ppm + glass producing a two point straight line calibration. Each sample's volume is adjusted to produce a calibration range interpolation value of concentration.

Calculations produce a concentration in the whole analyte via concentration in the glass and ash.

Mg, Al, Si, K, Ca, Ti, Fe, Sr, Ba

These metal's concentrations are determined using an energy dispersive X-ray fluorescence analyzer (ORTEC TEFA III) via a two-stage sample preparation.

The analyte is slowly heated to 750°C in air and maintained overnight. The ash is agate-ground to pass a 200 mesh sieve, and reashed.

Ash (1 g) and $Li_2B_4O_7$ (4.5 g) is then carefully weighed into a platinum crucible, mixed, and swirl-fused at 1050 C in a muffle oven. The glass is then weighed to determine the size of any small attendant loss on fusion.

The glass is then reheated to 1050 C and poured from the crucible into a preheated platinum mold cooling to form a glass disk having an even sample distribution throughout and an X-ray smooth surface.

The glass disk is placed in the sample tray of the X-ray fluorescence analyzer bracketed by standard samples. The 9 KV, 200 μA X-rays strike the

flat bottom surface of the sample ash in the $Li_2B_4O_7$ glass disk exciting all metals, except Sr and Ba, to emit in our detector's visible range.

The background of peak tailing and glass disk reflection is overtopped by element specific peaks whose area is proportional to concentration. Concentration per peak area and interelement effects are determined by analyzing glass disks made with reference materials showing only one or two element peaks.

Each sample glass disk is run bracketed with well characterized standards having a compositional variation designed to place our sample's elemental concentration within their range.

The Ba and Sr analysis is similarly carried out but at greater excitation conditions of 50 KV and 2 μA. The samples are then run with a suite of known concentration samples from which a least squares linear regression furnishes the analyte concentration.

F, Cl, Br

These concentrations are determined using an oxygen bomb method to combust the sample. The volatile anions are trapped in an alkaline solution, then the appropriate specific ion electrode as an Orion 901 analyzer is used to potentiometrically determine these anions.

A 1 g sample is combusted in a Parr bomb platinum crucible at 25 ± 5 atmospheres of oxygen and electrically ignited. The anion scavenging solution in the bomb is alkaline (Na_2CO_3 for Cl^- and Br^-, NaOH for F^-) and made up to at least 50 mL via washing the interior surfaces of the bomb.

An ionization buffer is added to the solutions (KNO_3 for Cl^- and Br^-, TISAB III for F^-) which aids in developing a more linear calibration curve of specific ion electrode potential versus standard concentrations.

As, Se, Sb

The method used by Analysis and Standardization to determine these concentrations is advantageous in that these metals produce gaseous hydrides which can be quantitatively decomposed in an atomic absorption spectrophotometer cell.

A .5 g air dried sample is weighed in a porcelain crucible, mixed with 1.5 g of Eschka mixture (MgO and Na_2CO_3), and heated slowly to 750°C under air. After 2 hours at this temperature, the sample is cooled and the

crucible is washed out with 25 mL water and 20 mL concentrated hydrochloric acid into a 0.1 L Nalgene volumetric flask.

Hydrochloric acid is used to dissolve the Eschka ash ensuring that the metals are in the correct oxidation state by the reaction:

$$SeO_4^{2-} + 2\ HCl \qquad SeO_3^{2-} + H_2O + Cl_2$$

The antimony technique is very similar with the addition of 3 g of tartaric acid as a complexing agent and 4 mL KI/NaOH solution as a reducing agent (0.1 kg KI and 2 g NaOH/L of solution).

A varying, well known, sample volume is then introduced into the reaction vessel in order to produce an absorbance within the calibration range. On make up to a reaction volume of 20 mL $LiBH_4$ solution is introduced producing the metal hydride.

The metal hydride is flushed out of the reaction vessel with argon into an optical quartz cell in the atomic absorption spectrophotometer's light path. Gas entering at the centre of the cylindrical cell is rapidly heated to 900°C producing analyte atoms with a residence time of seconds before leaving the cell near the cylinder's ends.

Standard samples calibrate the system bracketing each analytically determined concentration.

NEUTRON ACTIVATION ANALYSIS

The method used by our commercial laboratory is a standard technique based on the production of decaying short life radionuclides by neutron bombardment.

A sample of coal is heated to dryness then one gram accurately weighed into sealed plastic vials. A series of up to twenty is introduced on a tray into a CANDU pile where it receives about five minutes of thermal neutron bombardment.

The samples are let stand for a day then each is placed in a fine wire particle energy counter producing a spectrum of intensity versus emitted particle energy.

The spectrum is fed into a multichanneled region of interest computer program that assumes specific peak energy intensity is linearly proportioned to analyte concentration.

RESULTS

Samples were chosen to provide a good spectrum in coal quality and geographic location and submitted as routine samples to the Analysis and Standardization Section, Energy Research Laboratories, and Becquerel (Table 1).

Table 1 - Rank of samples submitted to laboratories A and E

Sample No.	Rank (by ASTM)	Sample No.	Rank (by ASTM)
1	Subbituminous Bs	23	Low-volatile bituminous
2	Low-volatile bituminous	24	Medium-volatile bituminous
3	Low-volatile bituminous	25	Low-volatile bituminous
4	Low-volatile bituminous	26	Low-volatile bituminous
5	Low-volatile bituminous	27	Low-volatile bituminous
6	Low-volatile bituminous	28	Medium-volatile bituminous
7	Subbituminous C	29	Medium-volatile bituminous
8	High volatile C bituminous	30	Medium-volatile bituminous
9	Subbituminous C	31	Medium-volatile bituminous
10	Low volatile bituminous	32	High-volatile C bituminous
11	Subbituminous C	33	High-volatile C bituminous
12	High-volatile C bituminous	34	Subbituminous A
13	Low-volatile bituminous	35	High-volatile C bituminous
14	Subbituminous C	36	High-volatile C bituminous
15	Subbituminous C	37	High-volatile C bituminous
16	Lignite A	38	Lignite A
17	Lignite A	39	High-volatile C bituminous
18	Lignite A	40	High-volatile C bituminous
19	Lignite A	41	High-volatile B bituminous
20	Lignite A	42	High-volatile A bituminous
21	Low-volatile bituminous	43	High-volatile C bituminous
22	Low-volatile bituminous		

These results were massaged into a moisture free whole coal basis in units commensurate with analyte concentration scale.

The laboratories were designated E for Energy Research Laboratories and A for Becquerel Laboratories.

Becquerel did not find concentrations of fluorine or phosphorus in our samples. Sulphur analyses were at, or below, detection limits as only a minor isotope of sulphur emits an analytically useful energy. This emission is not only weak but interferred with by the small amount of manganese found in our samples. Therefore fluorine, phosphorus, and sulphur were excluded from further consideration.

DISCUSSION

Graphical analysis was used to determine how closely Becquerel's Neutron Activation Analysis (NAA) correlated with our various methods (Table 2).

For each of the 15 elements a graph was accurately plotted with the abscissa as the Energy Research Laboratories concentrations (labelled E) versus the ordinate as Becquerel Laboratories concentrations (labelled A).

Becquerel's neutron activation analysis is published with precision values related to counting statistics and were too small to plot on the graphs.

These graphs have a set of common properties allowing useful information to be extracted. They are plotted with a maximum of 43 points with up to three outlier points deleted by inspection. From this statistically significant set a straight line is expected showing that both laboratories found the same concentration in each sample.

Linear regression analysis assumes a linear relation between the analyses for each element of the form $A = a E + b$ by minimizing each point's distance from the line developed by iteration (Table 3).

If both analyses were perfect for all samples, and all elements, we would expect both concentrations to be equal through the range including zero concentration. Thus the equation is of the form:

$$A = E$$

Table 2 - Dry, whole coal basis results of laboratories A and E

Sample No.	Lab	F ppm	Na ppm	Mg %	Al %	Si %	P %	S %	Cl ppm	K %
1	A		.299	.0911	0.897	1.12		<1.65	<20.3	<0.0212
	E	25.9	.258	.0650	0.871	1.18	.0087	0.1008	41.7	0.0074
2	A		.0867	.117	2.47	6.52		<1.36	24.6	0.385
	E	125	.0333	.076	2.40	6.07	.028	0.033	77.8	0.357
3	A		.242	.244	2.45	4.46		<2.07	135	0.113
	E	75.1	.222	.192	2.39	4.91	.038	0.175	104	0.117
4	A		.249	.737	7.66	18.6		<4.62	47.5	2.03
	E	111	.538	.791	7.64	18.9	.028	0.130	348	2.04
5	A		.088	.167	2.25	5.21		<2.15	304	0.257
	E	114	.077	.099	2.12	4.29	.035	0.118	125	0.227
6	A		.0710	.063	1.27	2.36		<1.83	380	0.050
	E	75.8	.067	.029	1.21	2.02	.036	0.076	149	0.043
7	A		.146	.199	0.696	1.79		<2.34	21.2	0.0275
	E	13.3	.127	.175	0.658	1.03	.0112	0.354	78.2	0.0225
8	A		.207	.256	2.88	7.29		<2.43	<16.4	0.273
	E	124	.221	.284	2.00	7.71	.0141	0.132	80.1	0.292
9	A		.499	.0584	0.610	1.01		<2.59	<27.5	<0.0226
	E	21.8	.454	.0555	0.581	1.00	.0274	0.324	47.5	0.0164
10	A		.251	.755	7.34	19.1		5.98	43.3	2.09
	E	244	.232	.773	7.42	18.3	.0084	0.146	496	1.99

Note: A = Neutron activation analysis by Becquerel Laboratories

E = Analysis and Standardization Section, Energy Research Laboratories

Table 2 - Cont'd

Sample Number	Lab	Ca %	Ti %	Fe %	As ppm	Se ppm	Br ppm	Sr %	Sb ppm	Ba %
1	A	1.10	.009	0.398	1.99	0.429	0.774	.0112	0.151	.0502
	E	1.10	.0027	0.410	2.19	0.11	3.03	.010	0.28	.0687
2	A	0.164	.110	0.441	9.21	2.75	6.54	.0058	1.05	.0435
	E	0.174	.134	0.438	8.47	2.64	4.62	.0066	0.98	.0475
3	A	0.687	.085	0.758	4.35	1.55	5.31	.0227	0.638	.0802
	E	0.740	.102	0.710	5.72	0.99	4.93	.0194	0.61	.0992
4	A	0.198	.278	2.95	196	7.02	2.30	.0179	7.11	.148
	E	0.270	.360	2.77	171	5.04	2.94	.0110	3.60	.174
5	A	0.393	.109	0.431	4.50	2.32	4.79	.0137	0.814	.0419
	E	0.360	.121	0.398	4.35	1.46	7.09	.0148	1.76	.0469
6	A	0.221	.074	0.201	2.05	1.30	5.08	.0129	0.474	.0421
	E	0.212	.083	0.198	2.10	0.99	4.42	.0149	0.73	.0408
7	A	0.981	.0209	0.582	1.90	0.795	2.13	.0232	0.0976	.0365
	E	0.989	.0190	0.578	1.62	0.80	4.69	.0128	0.27	.0513
8	A	1.09	.0888	0.662	4.68	1.01	0.290	.0174	0.767	.0672
	E	1.18	.0948	0.686	5.44	0.55	3.98	.0159	1.00	.0722
9	A	1.05	.0196	0.308	0.897	0.839	1.72	.0326	0.203	.0649
	E	0.881	.0236	0.322	0.53	0.86	1.07	.0000	0.33	.0000
10	A	0.235	.261	2.68	147	6.74	3.00	.0164	6.59	.153
	E	0.255	.335	2.70	148	4.09	2.29	.0108	4.02	.257

Table 2 - Cont'd

Sample No.	Lab	F ppm	Na ppm	Mg %	Al %	Si %	P %	S %	Cl ppm	K %
11	A		.0815	.315	2.10	7.31		<2.40	<15.3	.299
	E	82.2	.0748	.266	2.12	6.97	.0097	0.414	20.1	.292
12	A		.0459	.189	1.91	4.22		1.23	<11.4	.131
	E	40.3	.0396	.166	1.93	4.08	.0062	0.163	14.4	.116
13	A		.112	.0533	1.43	2.19		2.35	172	.0460
	E	51.9	.0890	.124	1.11	2.34	.0307	0.222	35.9	.0624
14	A		.132	.182	1.50	3.16		<1.73	37.8	.0723
	E	44.4	.143	.0638	1.87	3.48	.0355	0.134	14.2	.0473
15	A		.542	.118	2.35	3.86		3.93	<26.0	.132
	E	42.0	.483	.120	2.26	3.67	.0279	0.278	15.8	.146
16	A		.0997	<.0525	1.97	3.18		<1.70	241	.0797
	E	128	.0853	.272	2.17	3.02	.0402	0.176	56.0	.0855
17	A		.0816	.555	2.00	2.86		<2.85	<18.0	.134
	E	50.0	.0743	.500	1.97	2.75	.0422	0.692	20.7	.0860
18	A		.0483	.294	0.469	0.455		<2.07	<13.8	.0154
	E	18.9	.0467	.252	0.432	0.419	.0136	0.554	15.3	.0065
19	A		.250	.387	1.58	2.58		3.83	25.3	.0753
	E	27.3	.271	.331	1.44	2.36	.0604	0.514	15.8	.0496
20	A		.835	.310	0.677	1.19		<3.44	<33.9	.0625
	E	21.9	.667	.227	0.681	1.13	.0287	0.568	20.3	.0052

Note: A = Neutron activation analysis by Becquerel Laboratories

E = Analysis and Standardization Section, Energy Research Laboratories

Table 2 - Cont'd

Sample No.	Lab	Ca %	Ti %	Fe %	As ppm	Se ppm	Br ppm	Sr %	Sb ppm	Ba %
11	A	1.29	.0913	.539	7.87	2.08	0.584	.0087	1.75	.0636
	E	1.27	.128	.544	7.66	1.33	1.12	.0104	2.11	.0793
12	A	0.917	.0617	.729	1.24	1.39	<.177	.0201	0.423	.0272
	E	0.908	.0757	.742	0.88	0.38	0.91	.0212	0.73	.0140
13	A	0.308	.0654	.260	1.75	1.44	3.95	.0121	0.437	.0543
	E	0.702	.0344	.227	2.11	1.02	1.51	.0281	0.57	.0830
14	A	1.10	.0298	.323	0.996	2.20	1.90	.0356	0.330	.0857
	E	0.402	.0977	.360	0.58	1.13	0.89	.0184	0.57	.0924
15	A	0.854	.0294	.427	1.16	2.05	1.32	.0282	0.554	.0891
	E	0.895	.0366	.398	0.58	0.76	1.21	.0333	0.86	.0822
16	A	0.434	.0961	.196	0.623	1.67	6.91	.0180	0.402	.0504
	E	0.0554	.122	.188	0.24	0.75	14.1	.0000	0.60	.0000
17	A	2.35	.0759	.616	8.20	2.08	1.06	.0405	0.519	.0940
	E	2.31	.0784	.631	7.37	1.21	1.58	.0351	0.62	.121
18	A	1.46	.0196	.407	3.24	0.855	1.88	.0348	0.336	.0466
	E	1.53	.0196	.399	3.25	0.79	1.03	.0296	0.68	.0447
19	A	1.62	.0554	.336	2.11	1.00	1.30	.0641	0.861	.136
	E	1.64	.0538	.332	1.52	0.36	1.40	.0287	1.48	.134
20	A	1.41	.0467	.216	1.33	1.57	1.27	.0466	0.290	.0688
	E	1.31	.0494	.219	0.88	1.24	1.05	.0526	0.59	.0711

Table 2 - Cont'd

Sample No.	Lab	F ppm	Na ppm	Mg %	Al %	Si %	P %	S %	Cl ppm	K %
21	A		.731	.295	0.891	1.93		5.55	65.9	.0720
	E	30.5	.521	.260	0.808	.973	.0397	0.718	121	.0102
22	A		.0127	.0961	2.37	3.54		<1.21	45.9	.0204
	E	126.0	.0150	.0216	2.28	4.42	.0503	0.100	23.0	.0103
23	A		.00419	.0371	0.882	1.09		<0.931	13.0	.0164
	E	280.0	.0024	.0077	0.831	1.15	.257	0.0443	16.0	.0090
24	A		.00727	.0793	2.05	3.95		0.815	13.7	.238
	E	111.0	.0086	.0677	2.02	4.10	.0267	0.157	16.3	.218
25	A		.0132	.0857	2.10	4.56		<1.14	38.3	.125
	E	178.0	.0107	.0166	2.13	4.09	.0732	0.0533	16.1	.0985
26	A		.0193	.121	5.39	12.2		<2.81	44.3	.725
	E	295.0	.0142	.035	5.34	12.0	.0218	.0538	15.8	.523
27	A		.00641	.135	2.04	5.68		<1.32	<10.2	.207
	E	251.0	.0027	.102	2.01	5.12	.146	0.137	14.6	.196
28	A		.00734	.177	1.08	3.76		<1.02	26.6	.174
	E	136.0	.00510	.0580	1.70	3.85	.0413	0.193	14.3	.165
29	A		.0187	.170	3.34	7.93		<1.49	35.4	.437
	E	216.0	.0102	.0813	3.32	7.80	.0444	0.110	15.2	.411
30	A		.0789	.119	2.45	5.16		<1.92	18.6	.0868
	E	52.3	.0430	.0811	2.49	4.79	.0049	0.222	14.2	.0651

Note: A = Neutron activation analysis by Becquerel Laboratories

E = Analysis and Standardization Section, Energy Research Laboratories

Table 2 - Cont'd

Sample No.	Lab	Ca %	Ti %	Fe %	As ppm	Se ppm	Br ppm	Sr %	Sb ppm	Ba %
21	A	1.33	.0325	.398	3.07	0.669	1.16	.0466	0.605	.0763
	E	1.32	.0334	.390	4.35	1.12	0.92	.0456	1.09	.0687
22	A	0.238	.109	0.403	0.311	1.44	1.13	.0032	0.204	.0197
	E	0.264	.142	0.391	0.81	0.54	0.70	.0026	0.24	.0000
23	A	0.525	.0370	0.487	<0.155	0.796	<0.189	.0201	0.154	.0342
	E	0.527	.0465	0.501	0.58	0.78	0.60	.0205	0.19	.0355
24	A	0.315	.0995	0.258	0.469	2.07	0.336	.0108	0.609	.0222
	E	0.333	.128	0.247	1.05	1.75	0.63	.0111	0.55	.0000
25	A	0.231	.112	0.229	0.531	1.20	2.80	.0036	0.464	.0118
	E	0.254	.150	0.248	1.09	0.89	0.75	.0037	4.90	.0000
26	A	0.0744	.287	0.318	3.72	3.45	0.473	.00987	1.84	.0486
	E	0.137	.368	0.406	4.61	2.77	0.65	.0032	0.64	.0000
27	A	0.476	.0903	0.842	0.610	1.10	<.232	.0037	0.309	.0125
	E	0.528	.120	0.715	1.31	0.69	0.50	.0046	2.59	.0000
28	A	0.467	.105	0.294	0.796	1.91	0.511	.0117	1.09	.0287
	E	0.473	.139	0.304	1.53	1.50	0.55	.0116	0.44	.0000
29	A	0.297	.192	1.77	1.80	2.96	0.434	.0082	1.61	.0334
	E	0.358	.238	1.68	2.57	2.55	0.55	.0070	1.59	.0000
30	A	1.43	.135	0.186	0.883	1.48	<0.260	.0306	0.647	.0698
	E	1.47	.159	0.213	1.75	1.07	0.58	.0253	0.90	.1255

Table 2 - Cont'd

Sample Number	Lab	F ppm	Na ppm	Mg %	Al %	Si %	P %	S %	Cl ppm	K %
31	A		.0649	.262	2.68	4.00		1.41	13.0	.0516
	E	30.8	.0387	.199	2.56	3.77	.0000	0.224	12.6	.0460
32	A		.0201	<.114	0.883	2.46		<9.00	236	.121
	E	400.0	.0138	.0408	0.984	2.46	.140	0.394	29.3	.136
33	A		.0146	.0799	0.722	1.84		4.15	185	.162
	E	244.0	.0072	.0854	0.805	1.82	.0554	0.140	29.4	.185
34	A		.0426	.137	2.32	6.33		<3.20	215	.673
	E	1456.0	.0372	.0734	1.43	3.45	.100	0.150	750	.272
35	A		.122	.278	3.26	6.59		5.28	1401	.468
	E	244.0	.114	.184	3.32	6.11	.0413	0.292	1679	.372
36	A		.0416	.111	1.53	2.63		<5.27	1387	.368
	E	132.0	.0363	.0914	1.50	2.35	.0007	0.121	1423	.295
37	A		.102	.284	1.84	4.91		<7.84	1468	.162
	E	335.0	.0961	.160	1.53	4.49	.0119	0.868	2007	.127
38	A		.609	.904	4.56	9.49		<8.62	946	.505
	E	236.0	.588	.749	4.88	10.5	.0164	0.652	858	.487
39	A		.119	.0659	0.422	1.14		<7.86	3385	.0462
	E	84.0	.104	.0432	0.456	1.05	.0385	0.186	2775	.0406
40	A		.0218	.0550	0.952	1.58		<6.14	2016	.149
	E	86.0	.0230	.0411	0.938	1.33	.0070	0.0729	2798	.141

Note: A = Neutron activation analysis by Becquerel Laboratories

E = Analysis and Standardization Section, Energy Research Laboratories

Table 2 - Cont'd

Sample Number	Lab	Ca %	Ti %	Fe %	As ppm	Se ppm	Br ppm	Sr %	Sb ppm	Ba %
31	A	0.421	.150	0.438	0.698	1.15	0.346	.00477	0.353	.0411
	E	0.474	.209	0.421	1.38	0.63	1.01	.0054	0.520	.0000
32	A	0.537	<.0429	10.1	301	5.94	3.16	<.0095	5.96	.00975
	E	0.637	.0672	9.75	297	2.34	0.50	.0000	2.11	.0000
33	A	0.372	.0401	6.94	205	3.06	1.73	.0084	7.38	.0100
	E	0.218	.0539	6.80	197	2.95	0.50	.0000	3.66	.0000
34	A	0.0880	.131	3.65	109	3.65	7.72	<.0029	6.46	.0236
	E	0.331	.0894	8.51	121	3.71	0.62	.0000	5.06	.0000
35	A	0.420	.0935	2.68	22.0	2.06	7.78	.0149	0.791	.0183
	E	0.421	.129	2.57	23.9	1.89	23.4	.0087	1.17	.0000
36	A	0.165	.0441	4.56	141	3.34	31.0	.0055	2.42	.0095
	E	0.153	.0682	4.66	140	3.95	8.55	.0000	1.84	.0000
37	A	1.31	.0837	2.15	7.74	.937	16.5	.0122	0.442	.0040
	E	1.27	.136	2.12	9.41	1.60	37.4	.0018	0.70	.0000
38	A	1.02	.304	5.95	15.1	2.95	9.28	<.0113	0.772	.0195
	E	1.06	.378	5.88	16.9	2.50	8.39	.0040	0.88	.0000
39	A	0.403	.0200	2.98	22.0	1.36	3.15	.0031	0.591	.0128
	E	0.283	.0321	3.03	27.1	1.21	5.04	.0030	1.00	.0000
40	A	0.185	.0331	4.62	154	3.66	44.3	.0058	2.53	.0050
	E	0.141	0455	4.83	169	4.47	17.1	.0000	1.87	.0000

Table 2 - Cont'd

Sample Number	Lab	F ppm	Na ppm	Mg %	Al %	Si %	P %	S %	Cl ppm	K %
41	A		.0210	.0470	.762	1.65		<4.87	920	.0785
	E	127	.0215	.0253	.724	1.25	.0053	0.0324	1290	.0950
42	A		.0389	<.174	.592	1.10		<11.8	1053	.0868
	E	98.2	.0400	.0807	.604	1.11	.0160	0.116	1526	.0919
43	A		.00966	<.123	.435	0.990		<9.48	1142	.0978
	E	97.6	.0878	.0182	.575	0.893	.0506	0.421	1327	.0723

Note: A = Neutron activation analysis by Becquerel Laboratories

E = Analysis and Standardization Section, Energy Research Laboratories

Table 3 - Linear regression results

A = (a ± 2Sa) E + (b ± 2Sb)					
Metal symbol	a	2Sq	b	2Sb	Coefficient of determination (r2)
Fe	1.0175	.0121	-0.0106	.0319	.9986
As	1.0132	.0241	-0.8608	1.90	.9945
K	1.0238	.0301	0.0164	.0148	.9921
Si	0.9913	.0311	0.1708	.185	.9904
Al	0.9845	.0397	0.0489	.1029	.9839
Ca	1.0099	.0446	-0.0153	.0391	.9827
Ti	0.7527	.0366	-0.0070	.0056	.9791
Na	1.1670	.0581	-0.0021	.0126	.9769
Mg	0.9787	.0774	0.0464	.0207	.9466
Cl	0.8653	.1114	9.5795	109.5	.8900
Ba	0.5978	.0364	0.0207	.0061	.8264
Sb	1.6178	.2881	-0.5855	.4861	.7630
Se	0.9100	.1838	0.5833	.4324	.7089
Sr	0.9675	.2320	0.0033	.0047	.6997
Br	0.6311	.2751	1.9564	2.85	.3687

or $A = (1.\dot{0})E + (0.\dot{0})$

$a = 1.\dot{0}$ (slope)

$b = 0.\dot{0}$ (intercept)

If one finds a non unity slope a systematic error is suspected in one of the two methods as one laboratory method indicates a consistently greater concentration than the other. This type of error is generally caused by a method calibration error.

If one obtains a non zero intercept the indication is that one method is very near its detection limit at the lowest concentrations. This means that in the lower part of the graphical range an interference causes a slightly positive concentration where a near zero concentration is expected.

In order to indicate how closely this calculated linear regression construct is to predicting each individual point a coefficient of determination is calculated. This value is equal to the ratio of the reduction in the sum of squares of deviations obtained by using the linear model to the total sum of squares of deviations about the sample mean, which would be the predictor of A if E were ignored.

n = number of points ion our sample set

$$S^2_E = \sum_{i=1}^{n} ((yi - (b + a\,xi))^2 / (n-2))$$

$$XVRYSM = \sum_{i=1}^{n} ((xi - \bar{X})^2)$$

$$a = \left(\sum_{i=1}^{n} (xiyi)\right) - \left(\left(\sum_{i=1}^{n} xi \sum_{i=1}^{n} yi\right) n^{-1}\right)\left(\left(\sum_{i=1}^{n} xi^2\right) - \left(\sum_{i=1}^{n} xi\right)^2 n^{-1}\right)^{-1}$$

$$2S_a = (\text{Student's t Statistic for } n-2)(S^2_E / XVRYSM)^{.5}$$

$$b = \left(\left(\sum_{i=1}^{n} yi\right) n^{-1}\right) - \left(a\left(\sum_{i-1}^{n} xi\right) n^{-1}\right)$$

$$2S_b = (\text{Student's t Statistic for } n-2)(S^2_E(n^{-1}+((\sum_{i=1}^{n} xi)n^{-1})^2 XVRYSM^{-1}))\cdot 5$$

$$SSE = \sum_{i=1}^{n} (A - \bar{A})^2 - a\left(\sum_{i=1}^{n} E_i A_i - \left(\sum_{i=1}^{n} E_i\right)\left(\sum_{i=1}^{n} A_i\ n\right)\right)^{-1}$$

$$CODET = \frac{\sum_{i=1}^{n} (A_i - \bar{A})^2 - SSE}{\sum_{i=1}^{n} (A_i - \bar{A})^2}$$

Thus the closer the calculated line is to predicting the raw data accurately the closer the coefficient of determination will be to unity.

With a sample set comprising more than 30 degrees of freedom one can assume a normal distribution of points about the calculated line whose spread is determined by the raw data. These normal curves can be used to determine error values of each element for concentrations over our range if one states that our confidence will be 95%. Thus we may state that we are 95% confident the concentration is within the calculated error values over this concentration range of common Canadian coal elements (Table 4). Critical Value for sample set size of Spearman's rank correlation coefficient at $\alpha = .025$, i.e., 95% confidence interval or two standard deviations.

Using the above calculations the slope and intercept errors can be calculated at a 95% confidence interval. The coefficient of determination is a measure of the calculated line's goodness of fit as it approaches unity from zero.

Table 3 lists the linear regression results on the basis of decreasingly accurate fitting equations (the parameters (a and b) error values reflect this).

The metal analyses can be divided into groups according to their being distinguishably deviating from and slope of unity and an intercept of zero.

The metal analyses showing a slope deviation from unity indicate a systematic error directly proportional to concentration such as a calibration or calculation error.

Table 4 - Neutron activation analysis of standards

Sample	1632A			1633A		
LAB.	NAA_1	NBS_2	$\frac{m_1 - m_2}{(S_1^2 n_1^{-1} + S_2^2 n_2^{-1})^5}$	NAA_1	NBS_2	$\frac{m_1 - m_2}{(S_1^2 n_1^{-1} + S_2^2 n_2^{-1})^5}$
Metal	$\% \pm 2S_1$	$\% \pm 2S_2$	/t/	$\% \pm 2S_1$	$\% \pm 2S_2$	/t/
Calcium	.25 ± .057	.23 ± .03	1.96	1.17 ± .19	1.11 ± .01	1.99
Iron	1.16 ± .079	1.11 ± .02	3.88	9.59 ± .59	9.4 ± .1	2.01
Magnesium	.15 ± .06			.40 ± .25	.455 ± .01	-1.39
Potassium	.40 ± .034	.42 ± .02	-3.21	1.91 ± .13	1.88 ± .06	1.33
Sodium	.0832 ± .0053	.0840 ± .0040	-.76	.168 ± .011	.17 ± .01	-.85

The metal analyses showing an intercept deviating from zero indicate a non systematic error as is produced by reporting results: below the method's detection limits; another element's interference concentration at low concentrations; or the analyte's concentration in a reagent chemical.

At very low coefficient of determination values not much can be said except that the author suspects both methods are at, or near, detection limits over our analyte range.

If we assume that ten samplings were taken to produce the grated 2s values we have a 95% chance of being correct if the t statistic is beyond 2.262 at zero.

Iron and calcium results by NAA for the National Bureau of Standard's 1632A standard coal sample are under suspicion of being inaccurate.

CONCLUSIONS

The neutron activation analysis analyte concentrations compare favorably with the methods presently used by the Energy Research Laboratories in the case of Fe, As, K, Si, Al, Ca, Se, Sr, and Br.

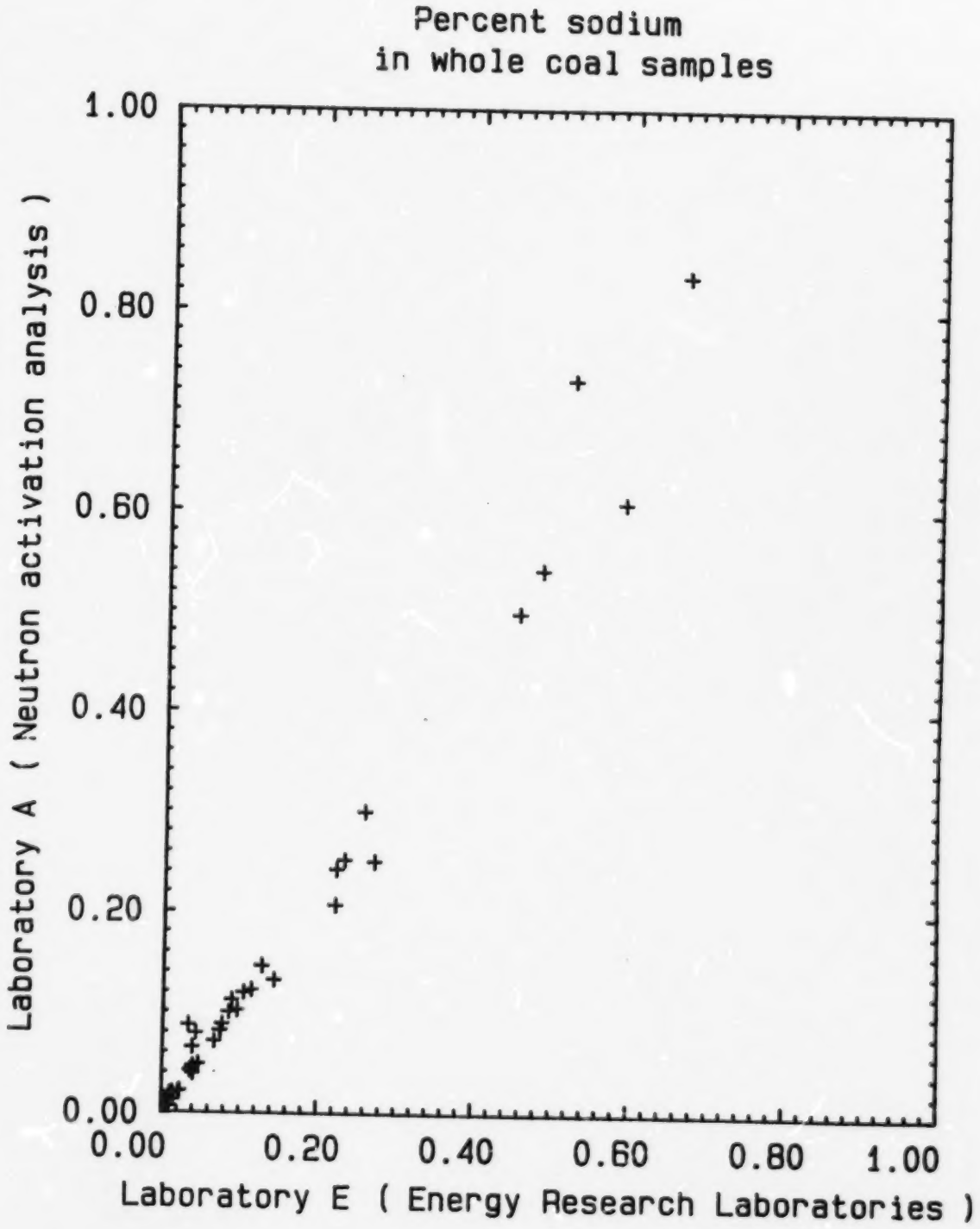
A systematic error showing direct concentration dependance is indicated in the following elements; Ti, Na, Cl, Ba, Sb.

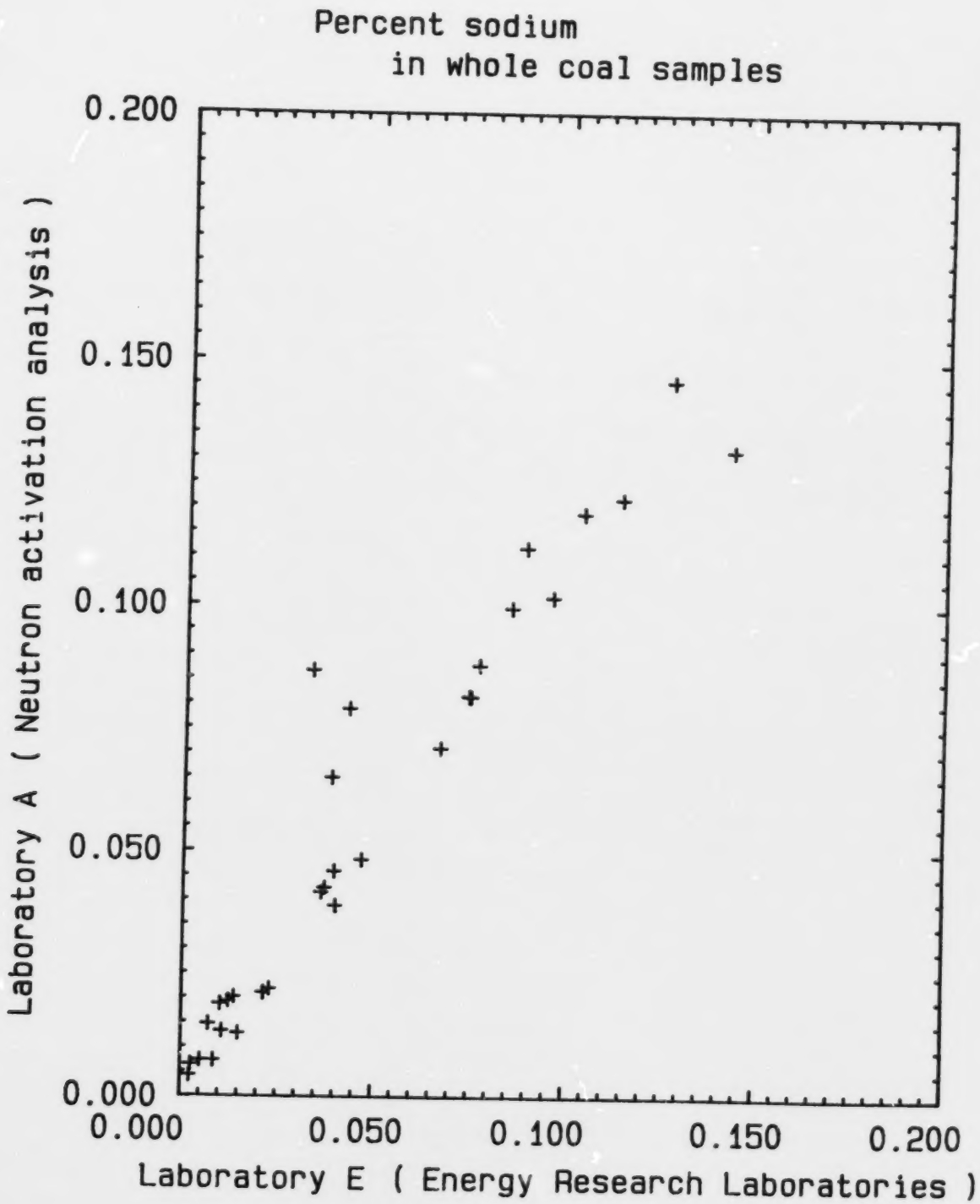
A non systematic error is indicated in the case at; Ti, Mg, Se, Ba and Sb.

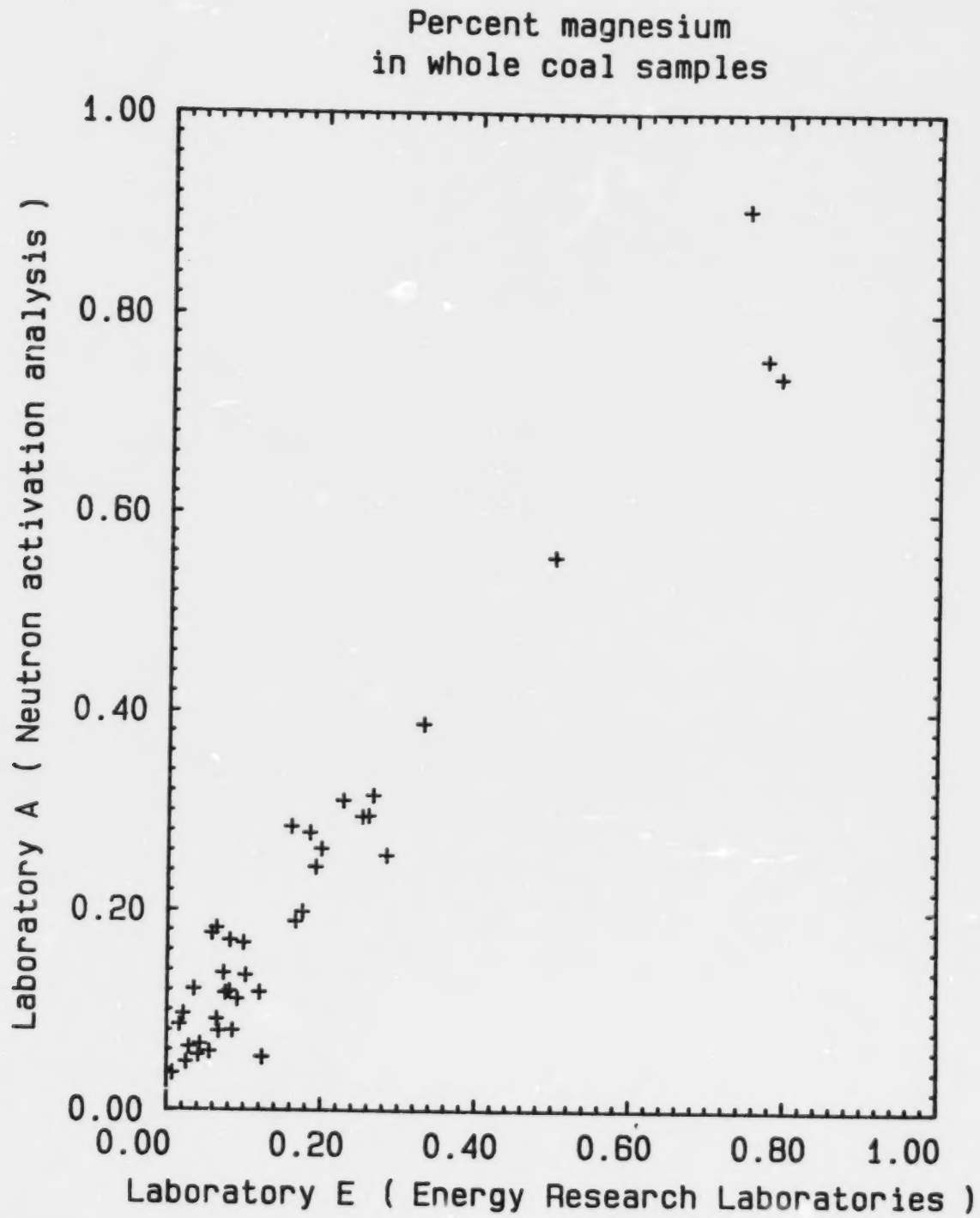
Further work is being undertaken to compare the neutron activation data with techniques currently in use or under study at ERL particularly with respect to trace elements with a view to using a similar correlational statistic format to localize and report method sources of errors and provide cross method precision data.

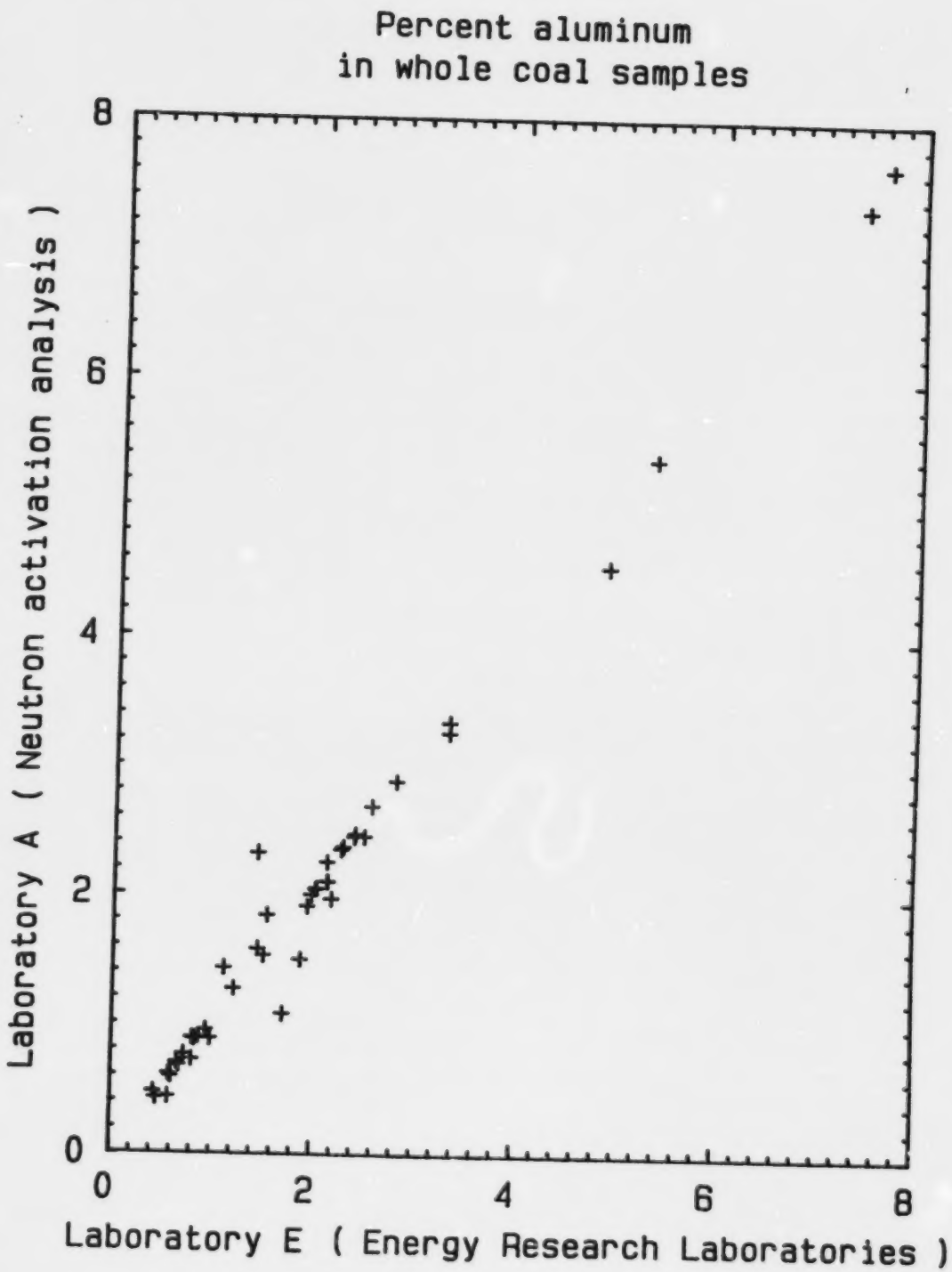
ACKNOWLEDGEMENTS

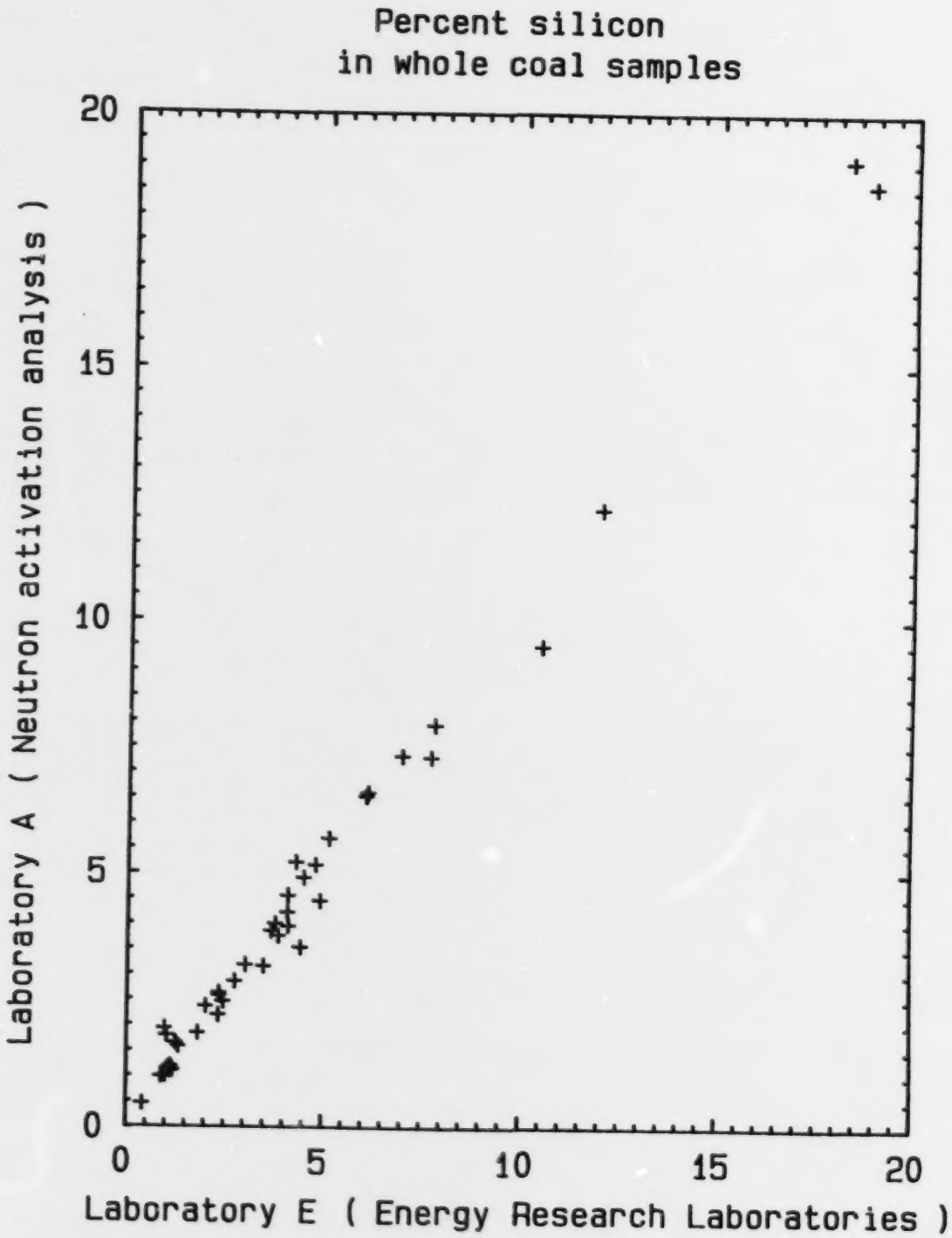
The support of Harry Barber, Louis Janke, Tim Moher and Jan Skulski, in the analysis and writing of this report is greatly appreciated.

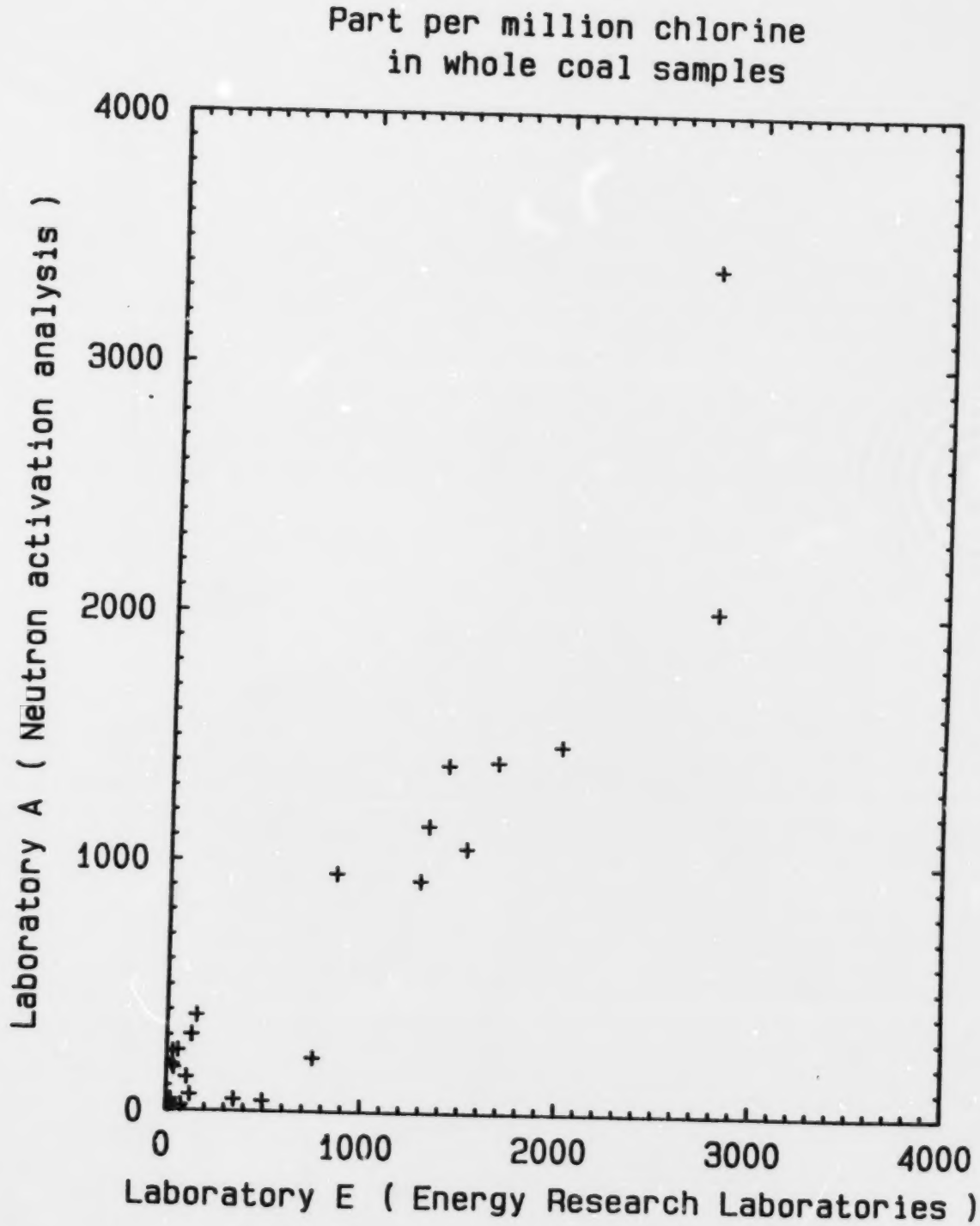

Percent sodium
in whole coal samples
Laboratory A (Neutron activation analysis)
1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
0.80
1.00
Laboratory E (Energy Research Laboratories)

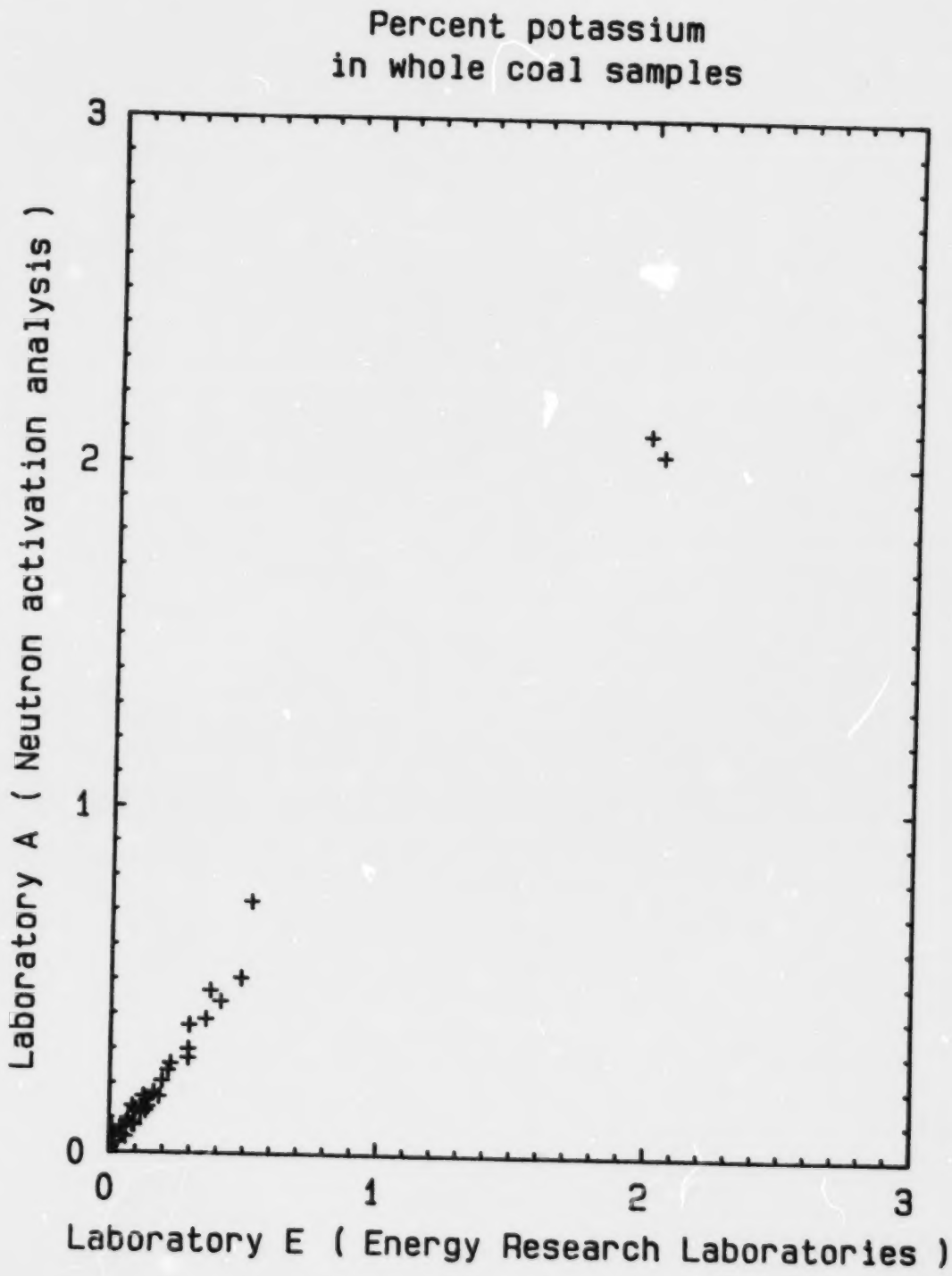

Percent sodium
in whole coal samples
0.200
0.150
0.100
0.050
0.000
0.000
0.050
0.100
0.150
0.200
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

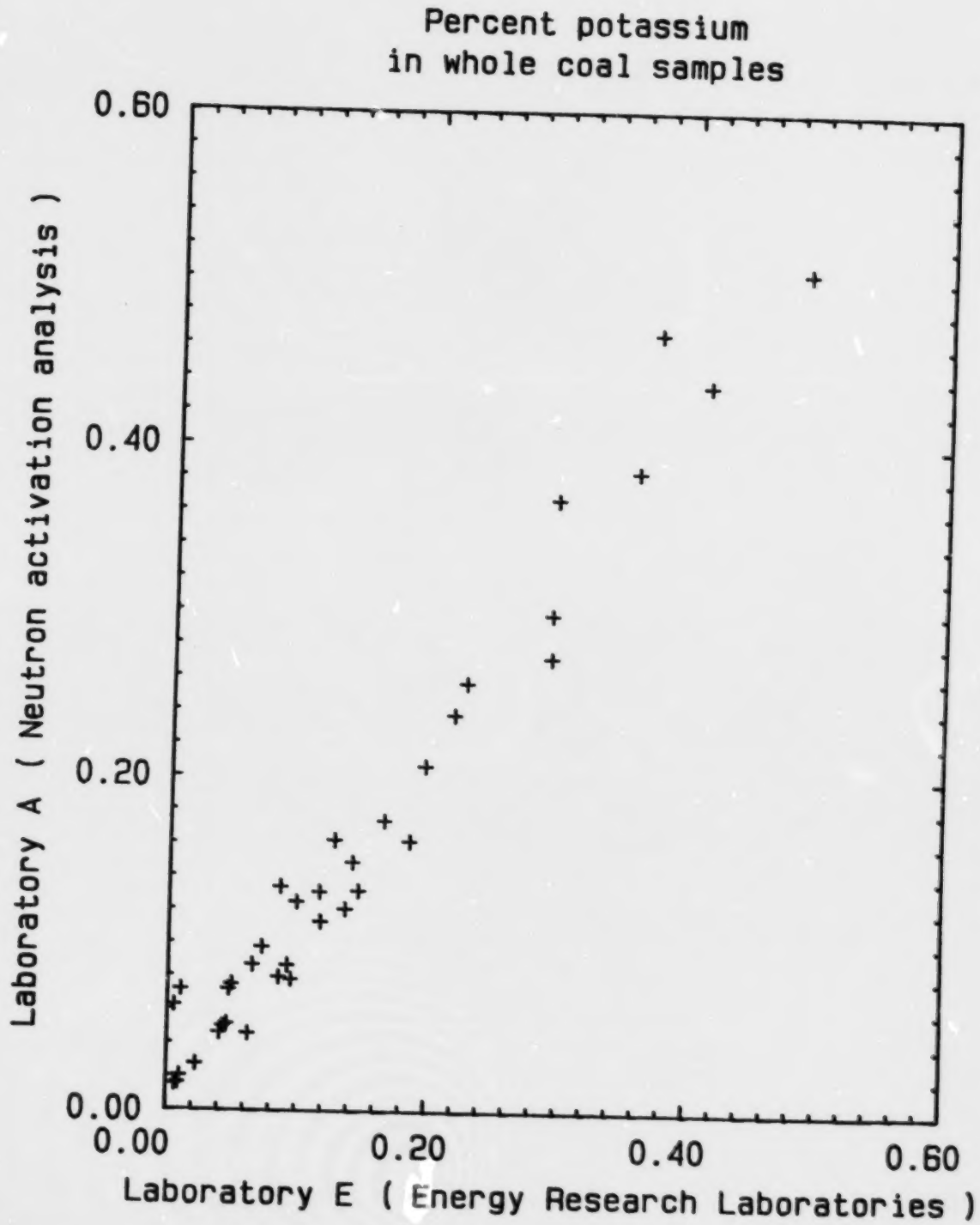

Percent magnesium
in whole coal samples
1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
0.80
1.00
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

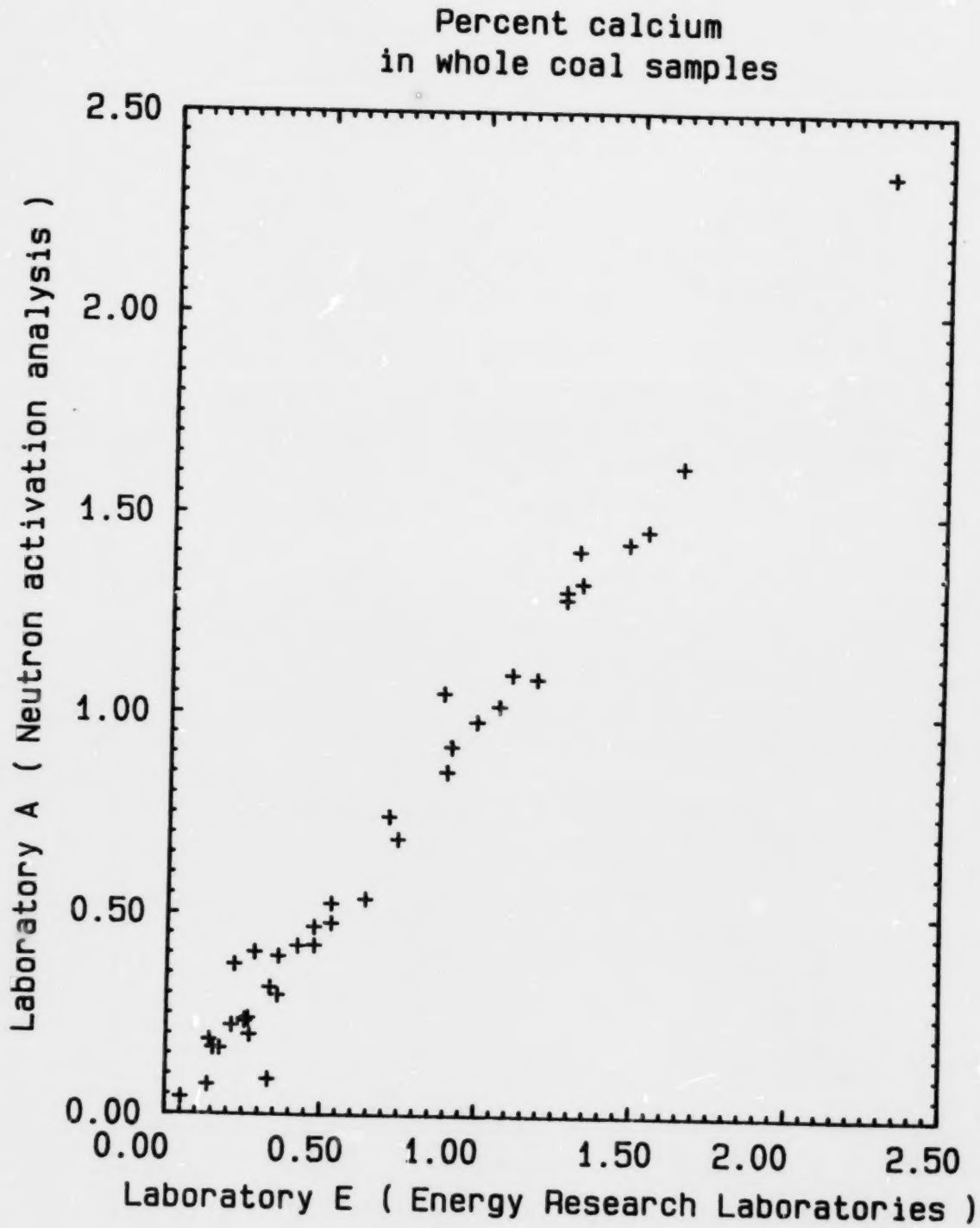

Percent aluminum
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8

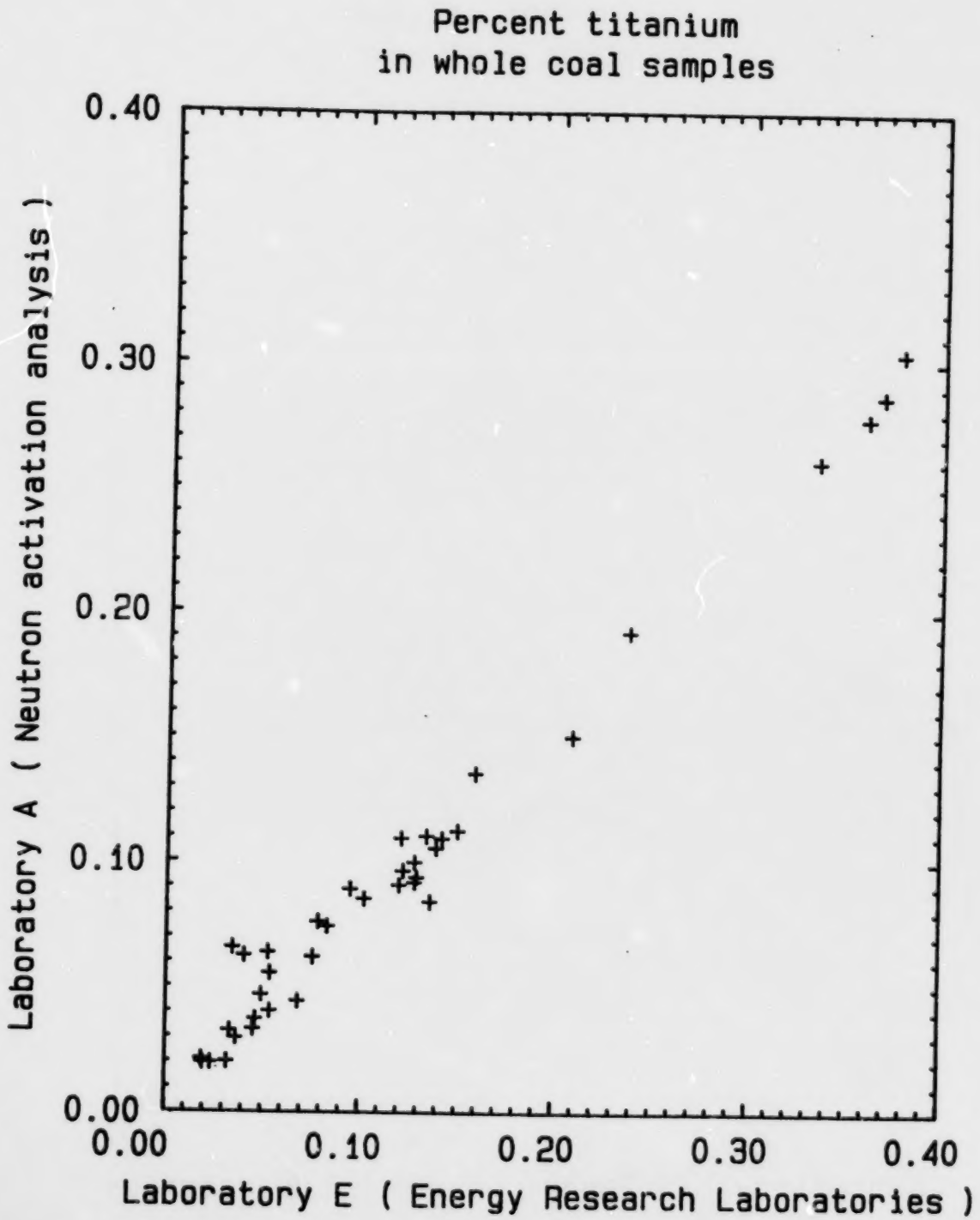

Percent silicon
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
5
10
15
20

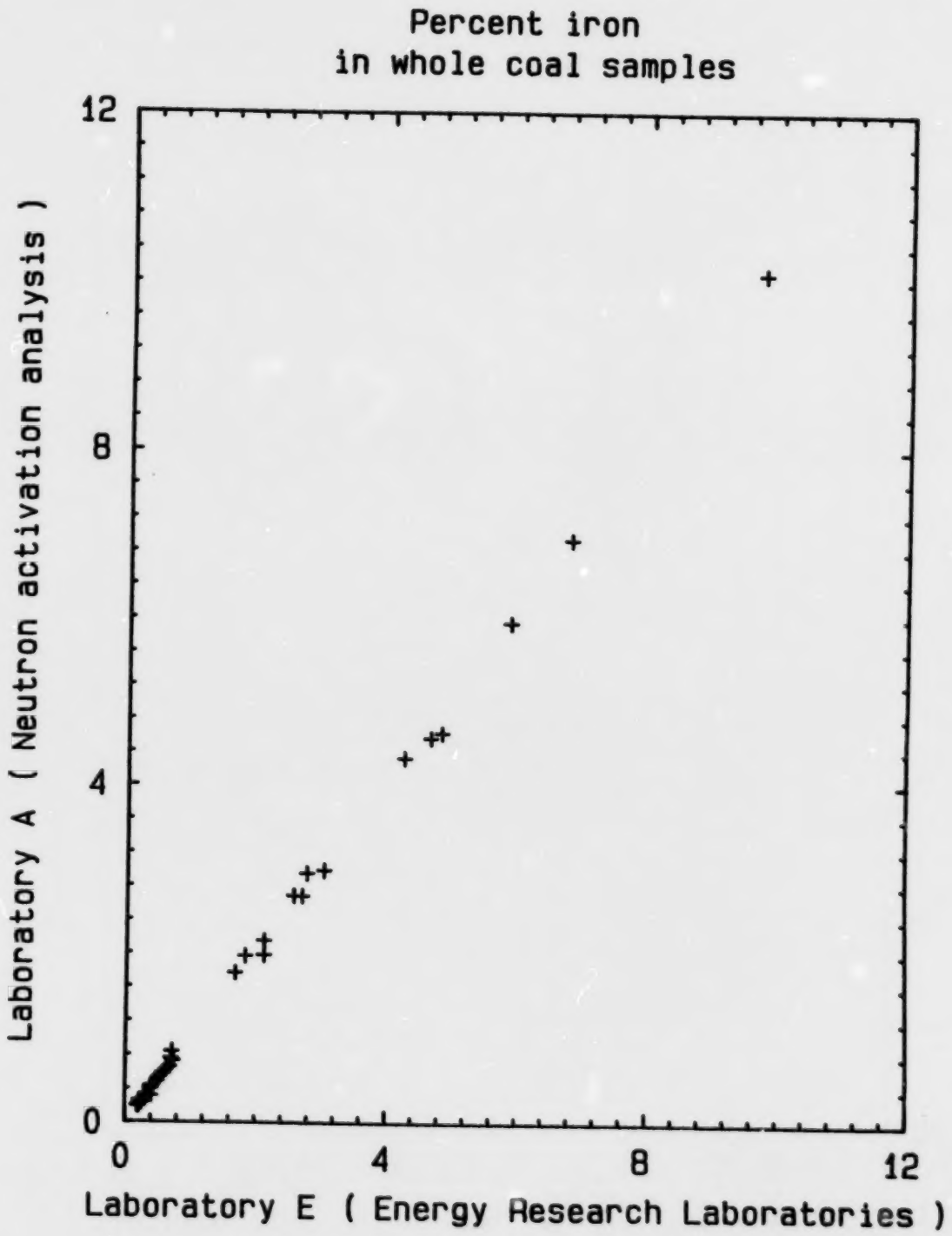

Part per million chlorine
in whole coal samples
Laboratory A (Neutron activation analysis)
4000
3000
2000
1000
0
0
1000
2000
3000
4000
Laboratory E (Energy Research Laboratories)

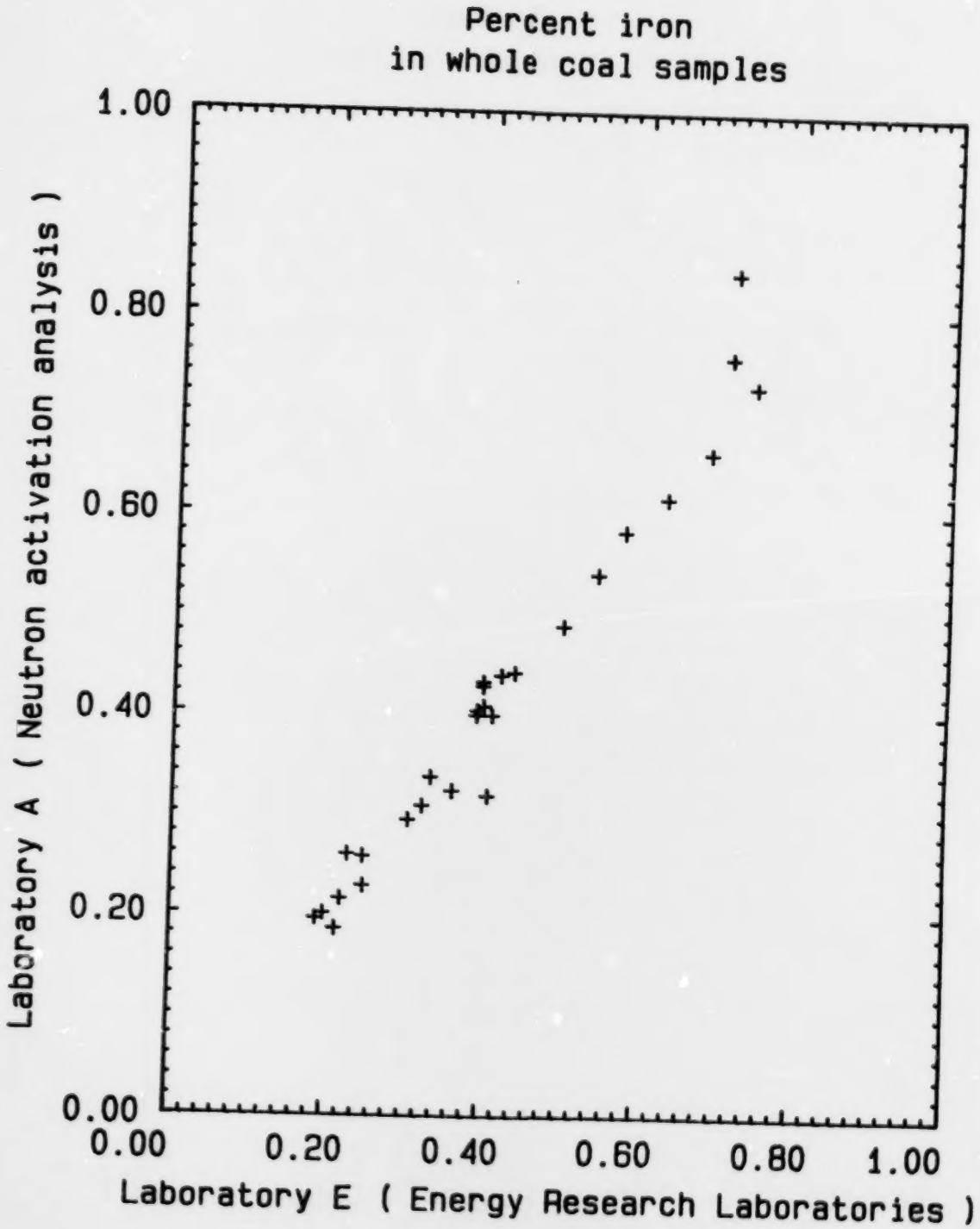

Percent potassium
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
1
2
3
0
1
2
3

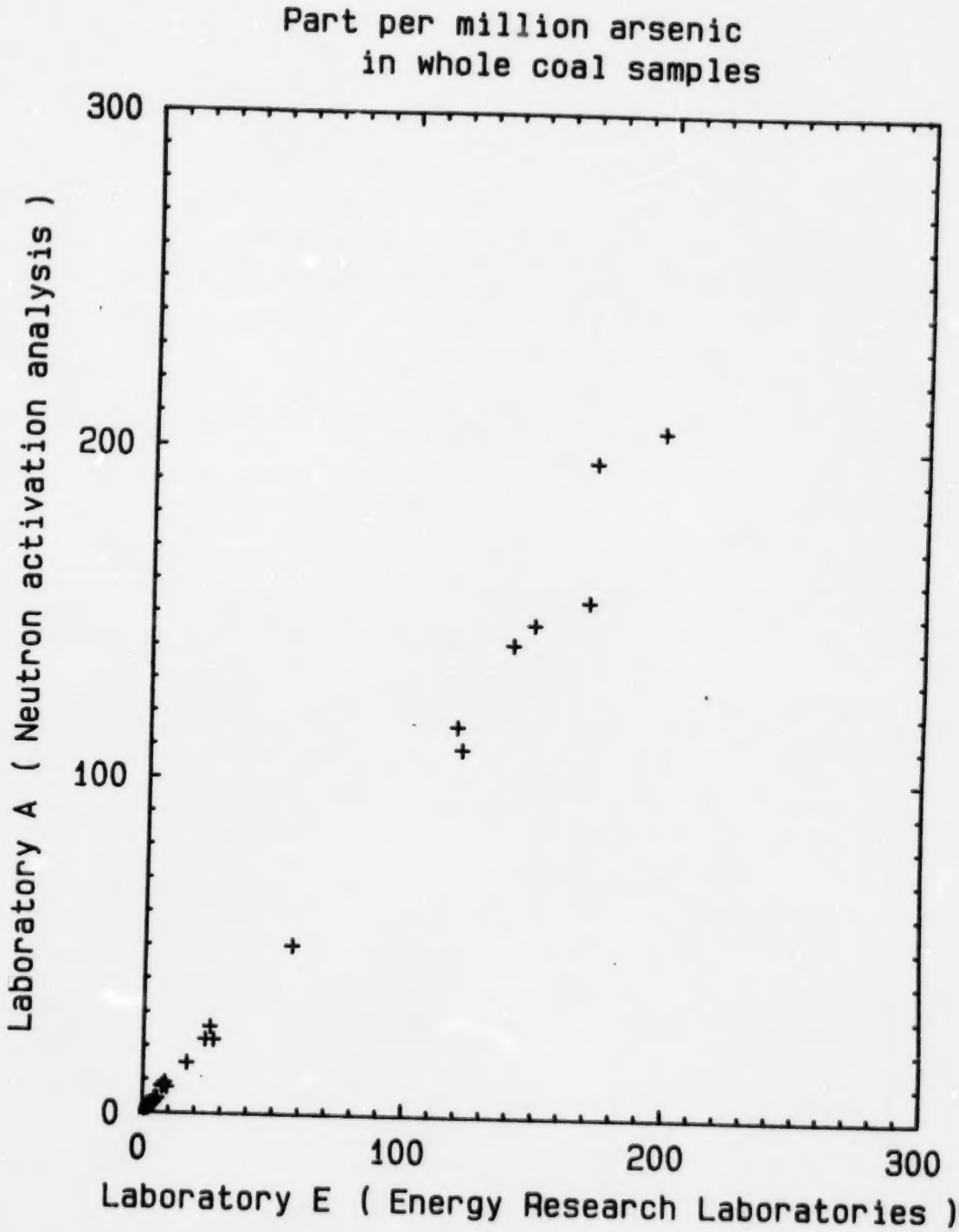

Percent potassium
in whole coal samples
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

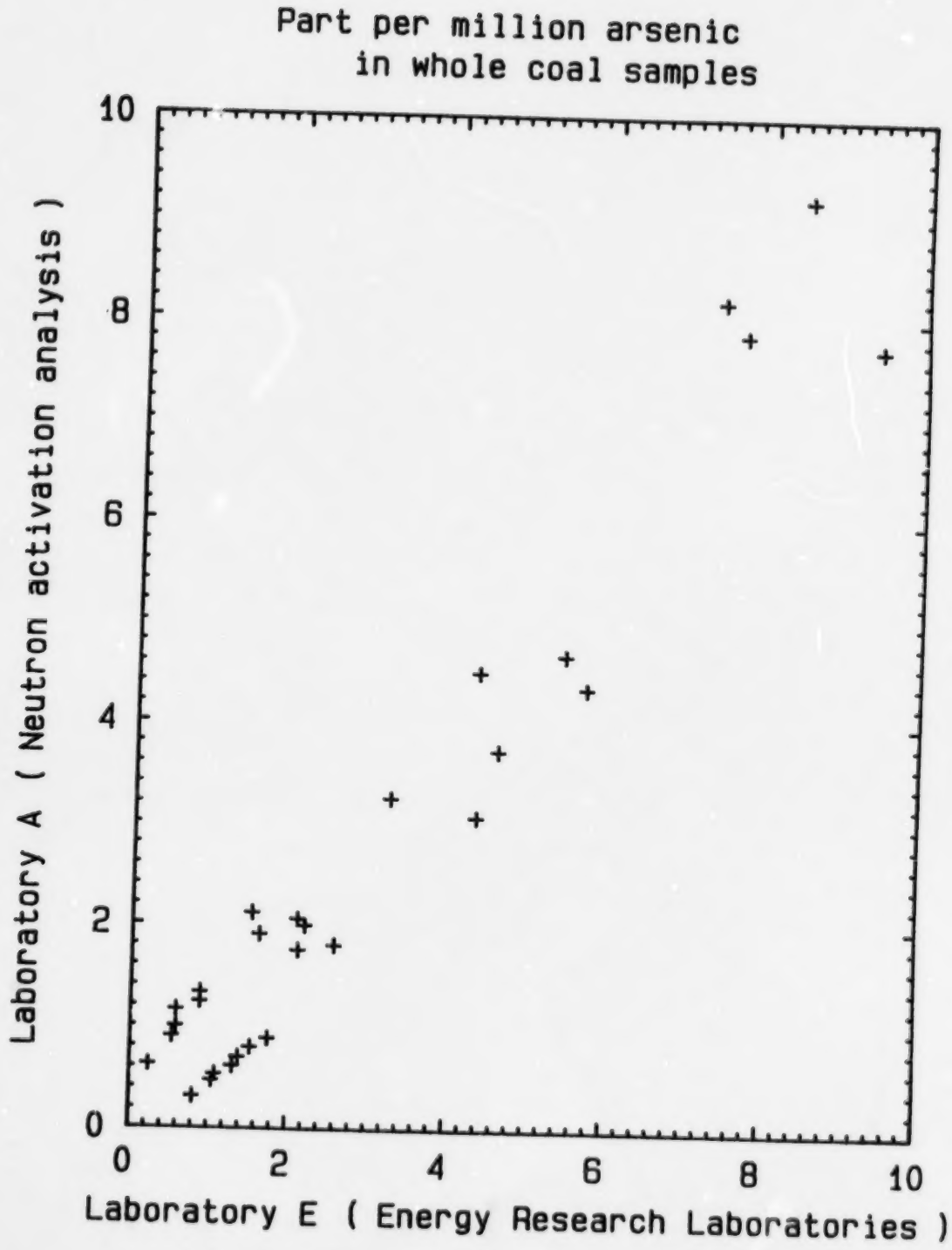

Percent calcium
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0.00
0.50
1.00
1.50
2.00
2.50

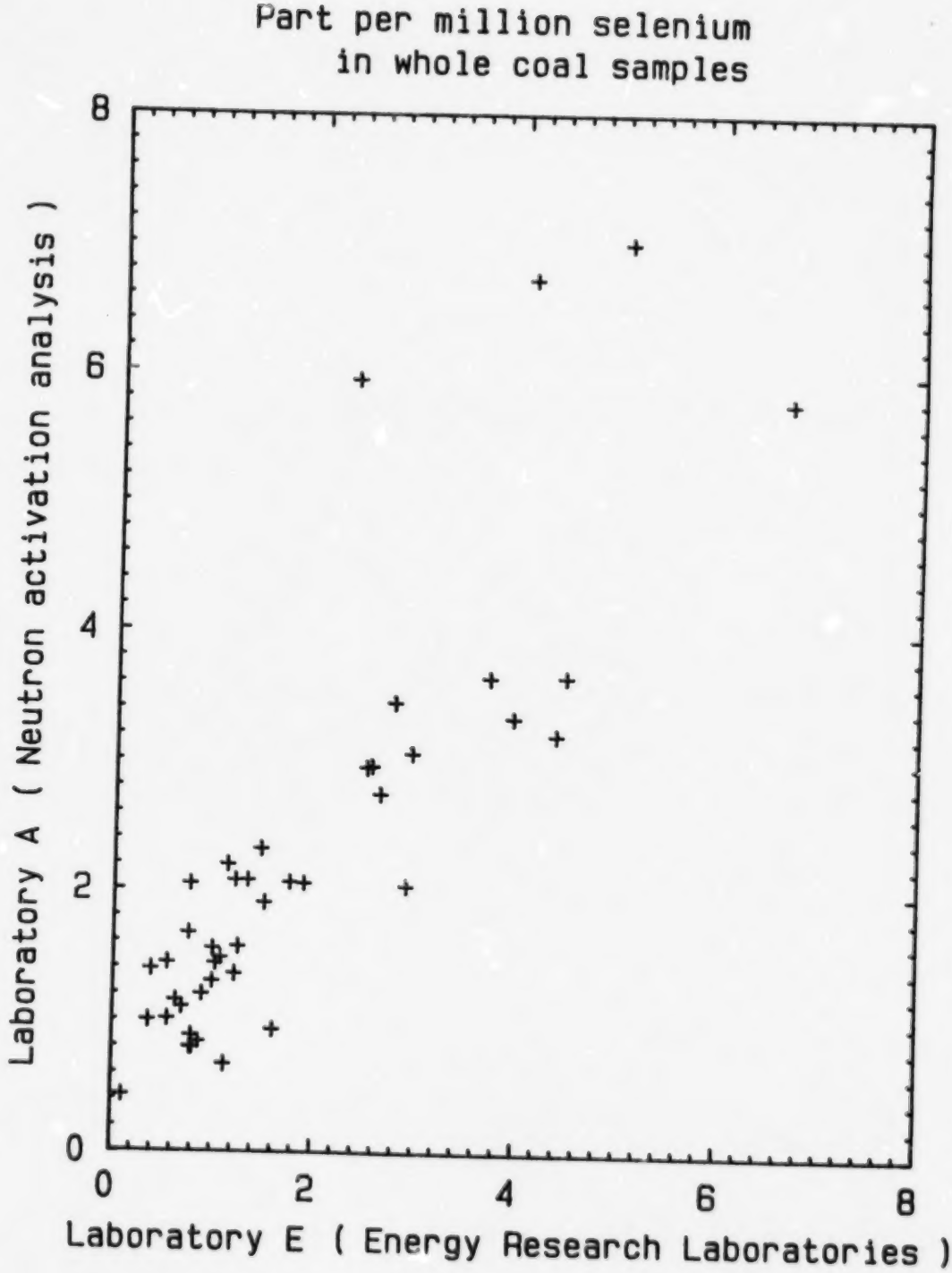

Percent titanium
in whole coal samples
0.40
0.30
0.20
0.10
0.00
0.00
0.10
0.20
0.30
0.40
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

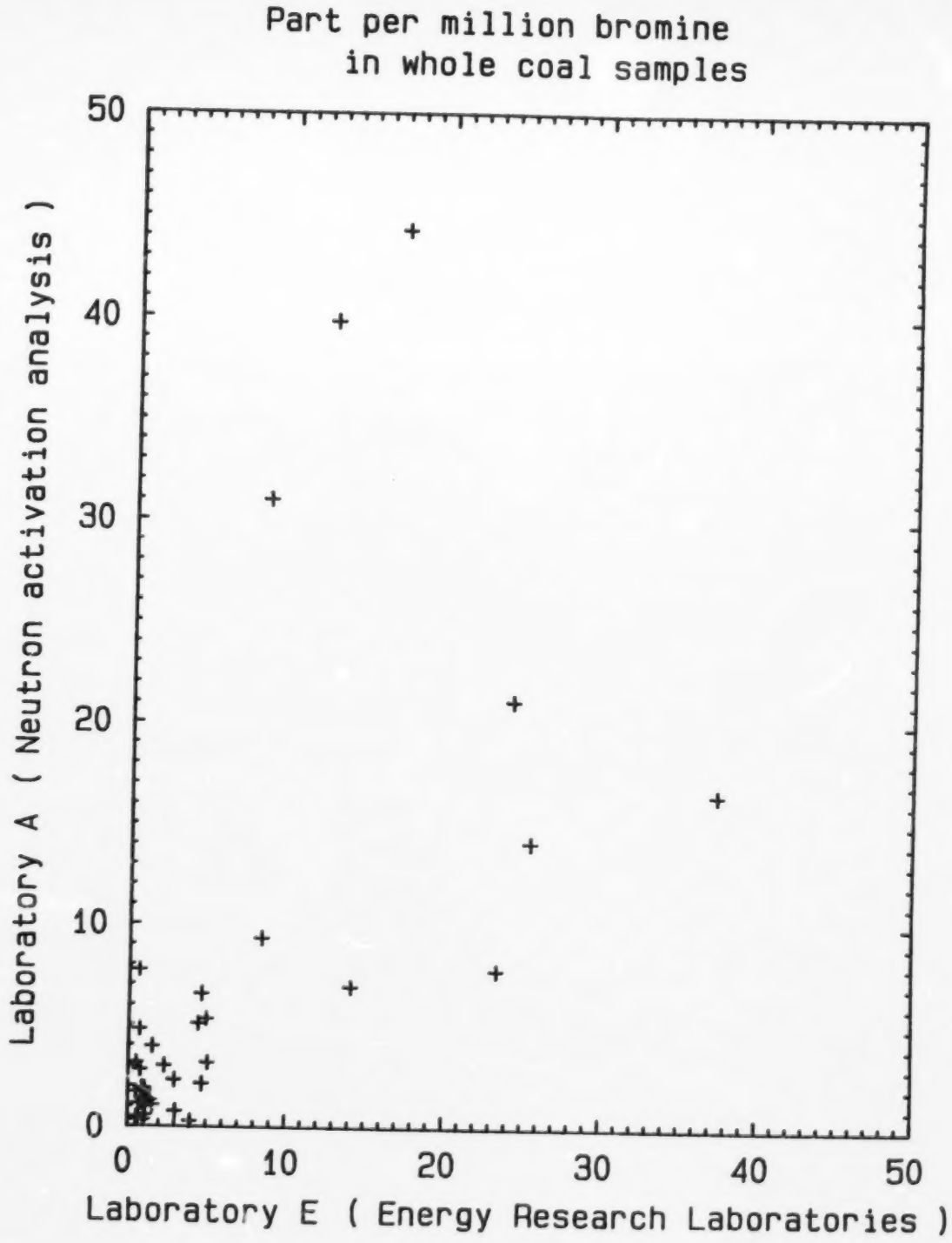

Percent iron
in whole coal samples
12
8
4
0
0
4
8
12
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

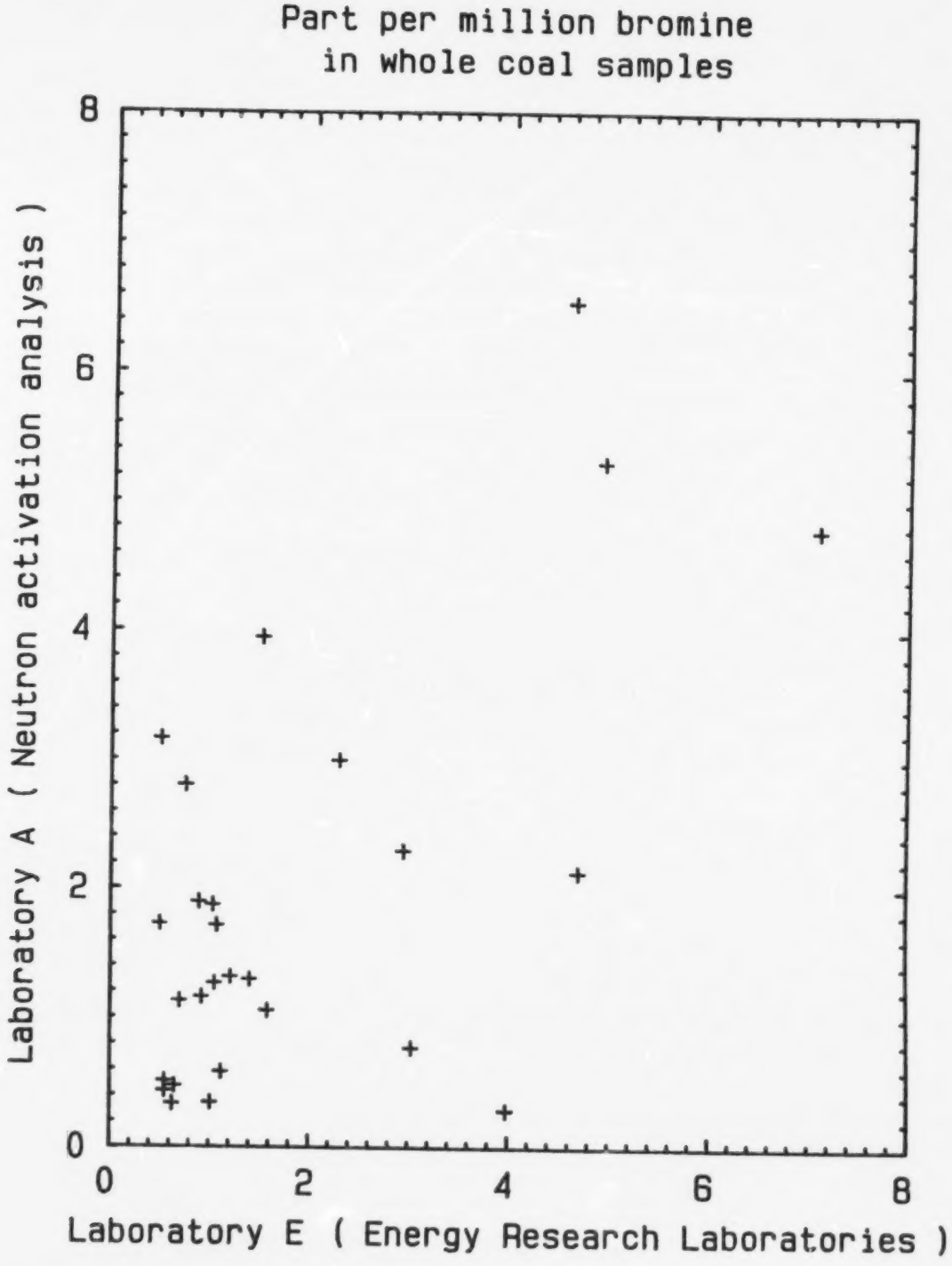

Percent iron
in whole coal samples
Laboratory A (Neutron activation analysis)
1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
0.80
1.00
Laboratory E (Energy Research Laboratories)

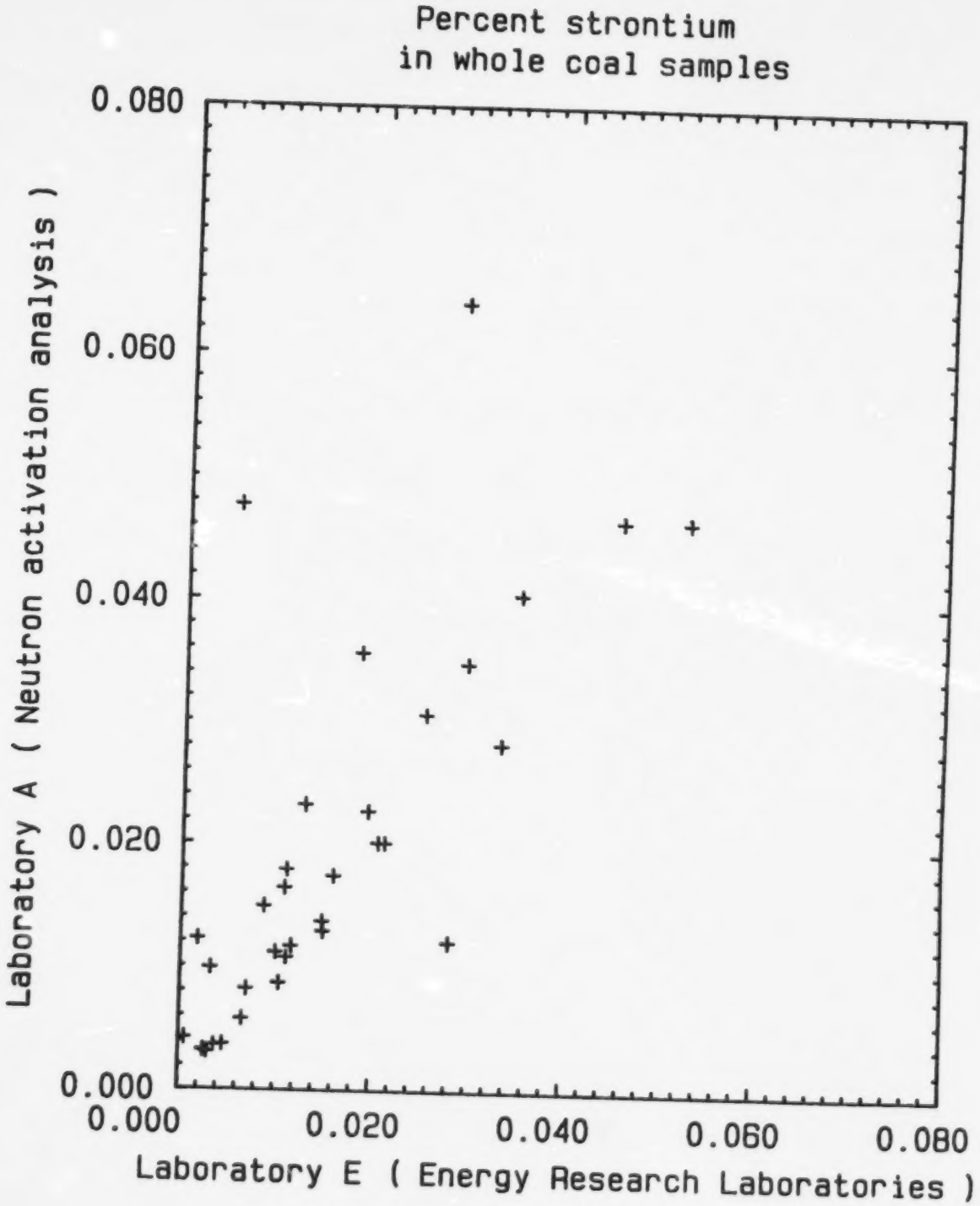

Part per million arsenic
in whole coal samples
300
200
100
0
0
100
200
300
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

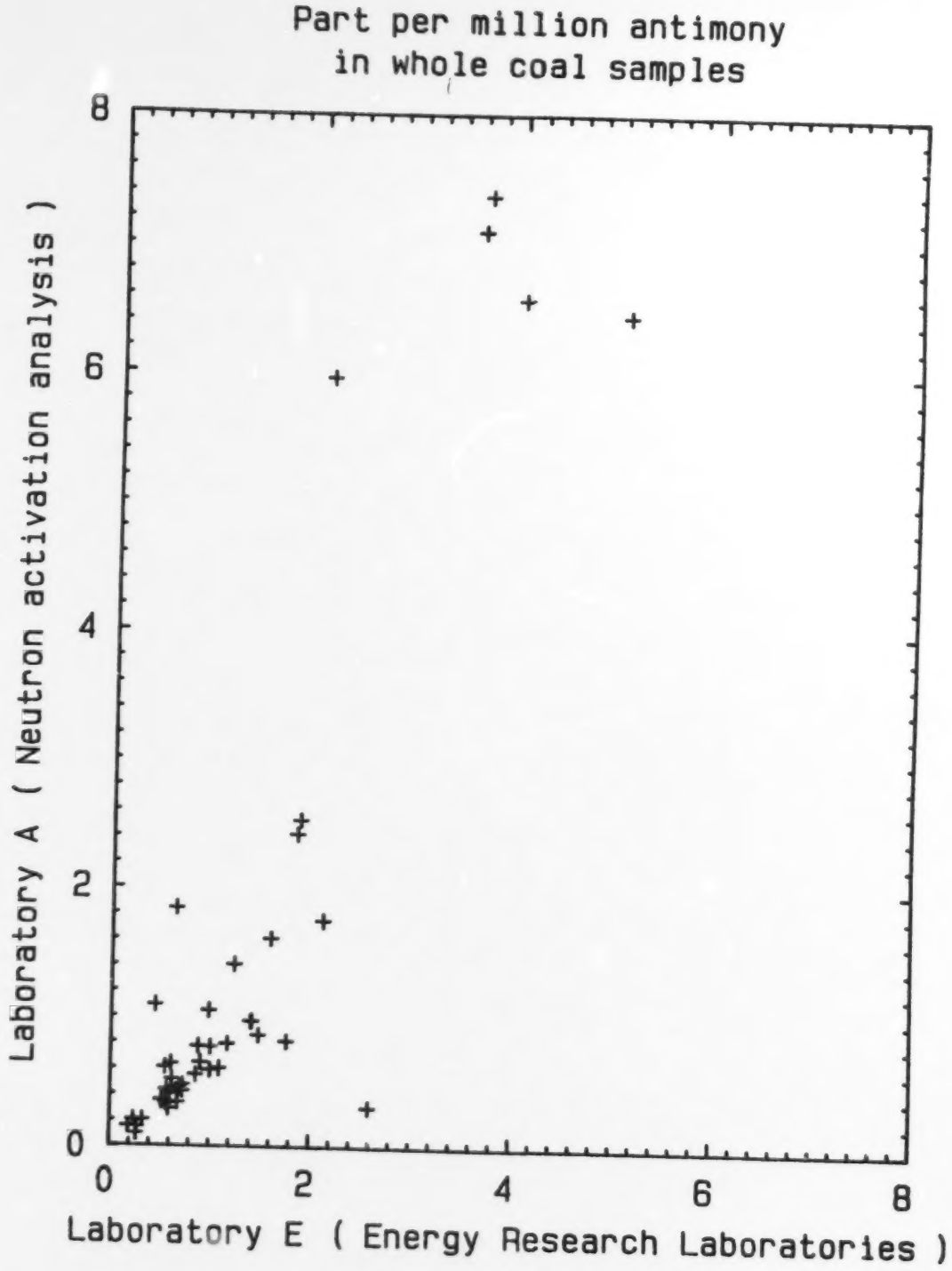

Part per million arsenic
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8
10

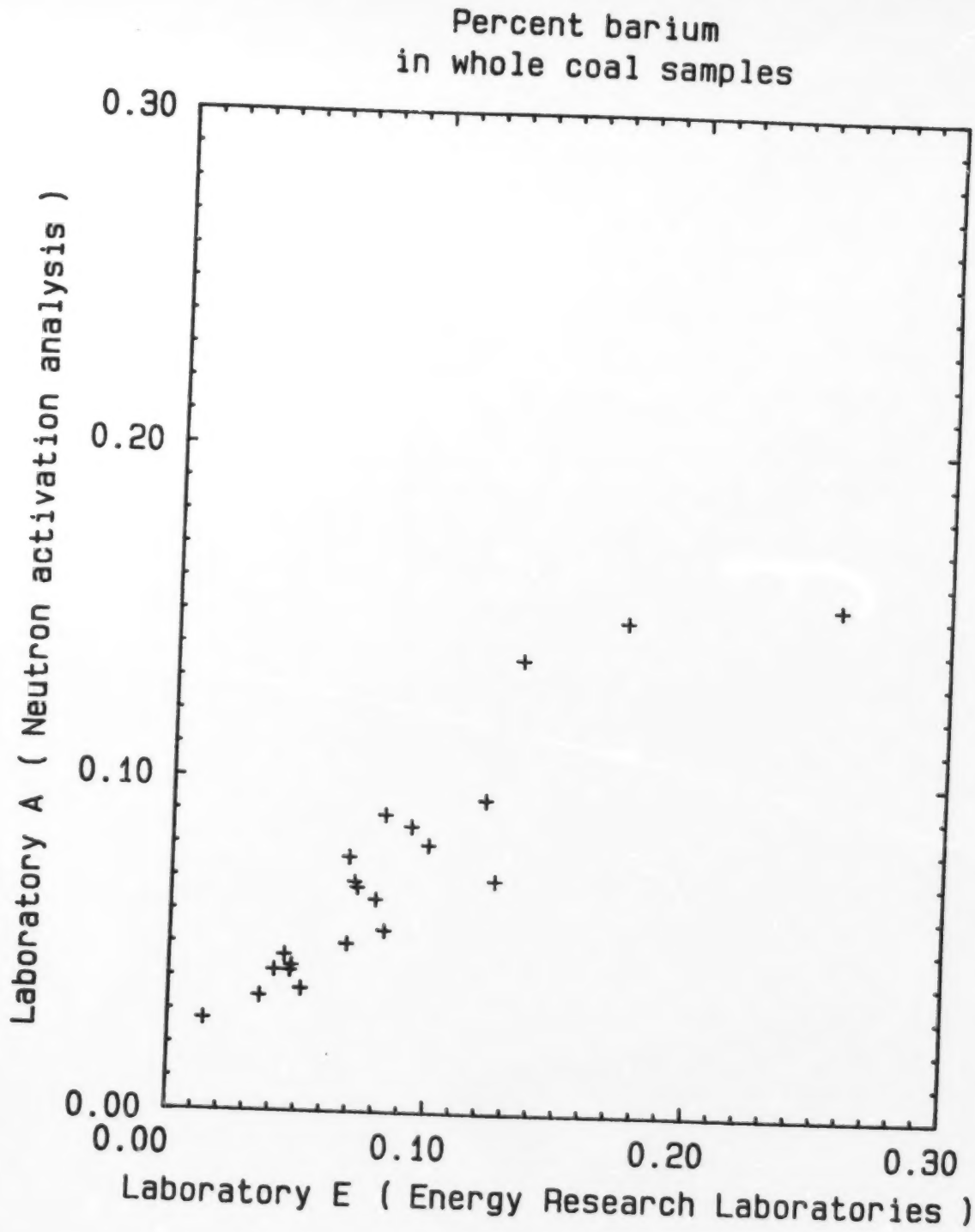

Part per million selenium
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8

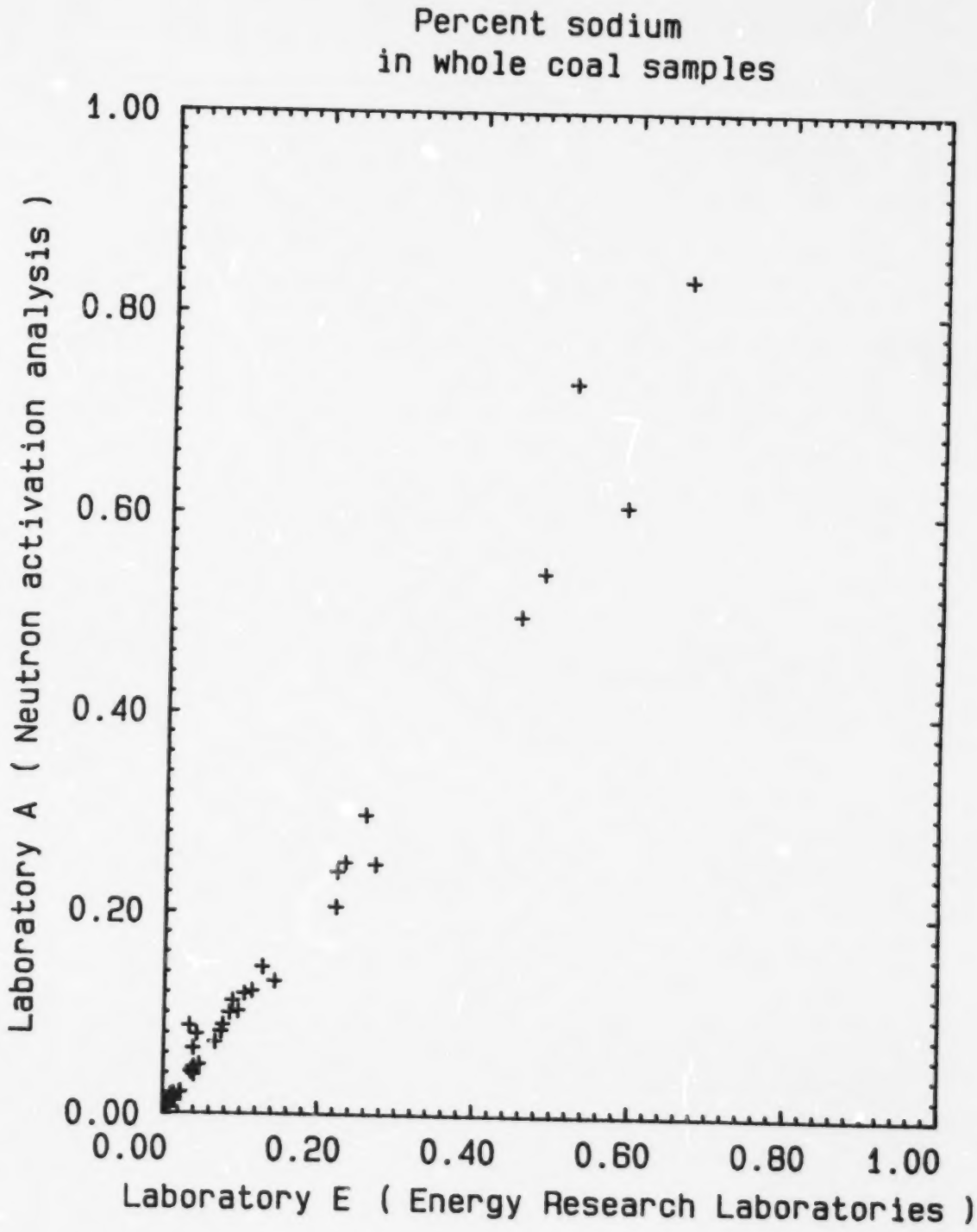

Part per million bromine
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
10
20
30
40
50

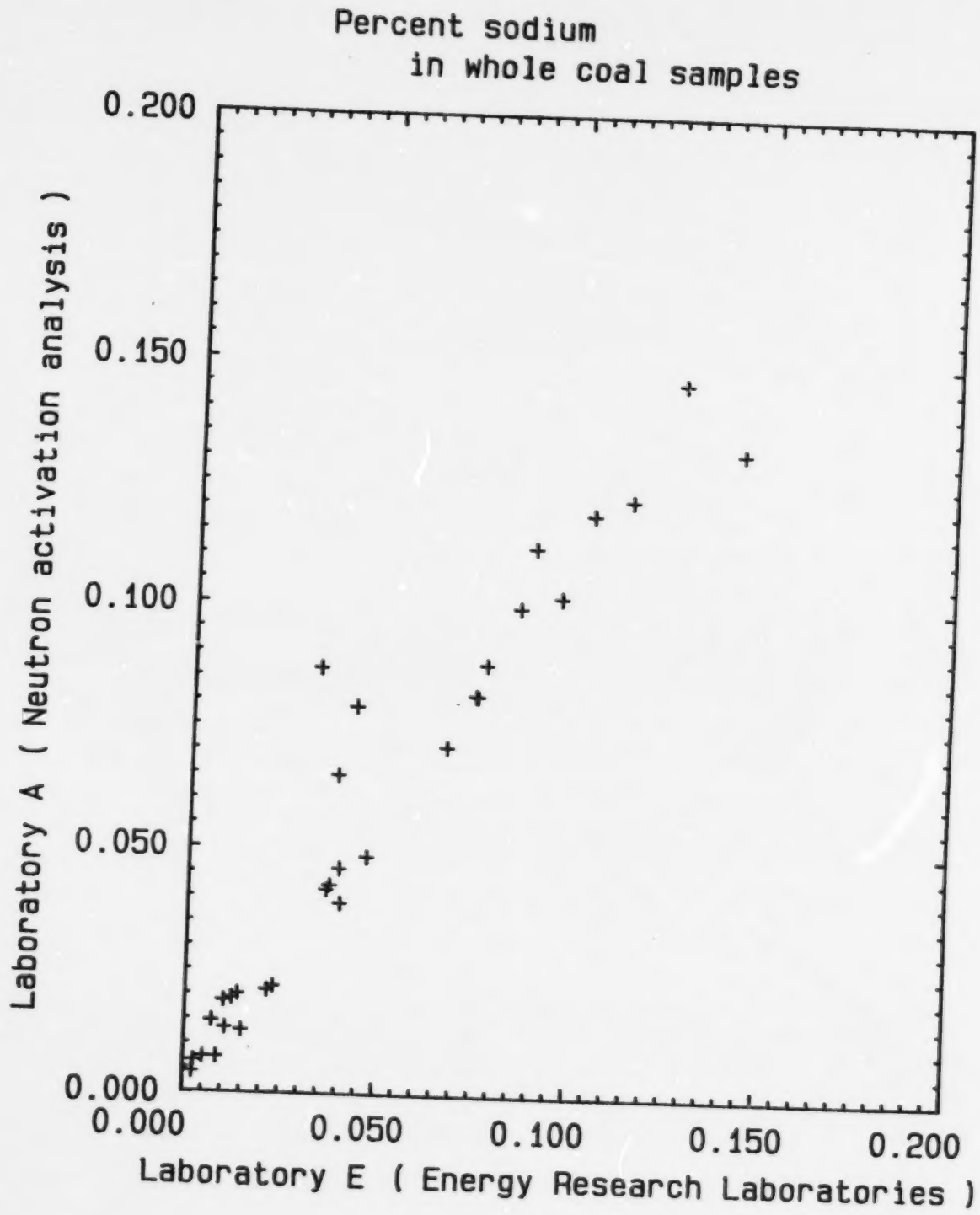

Part per million bromine
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8

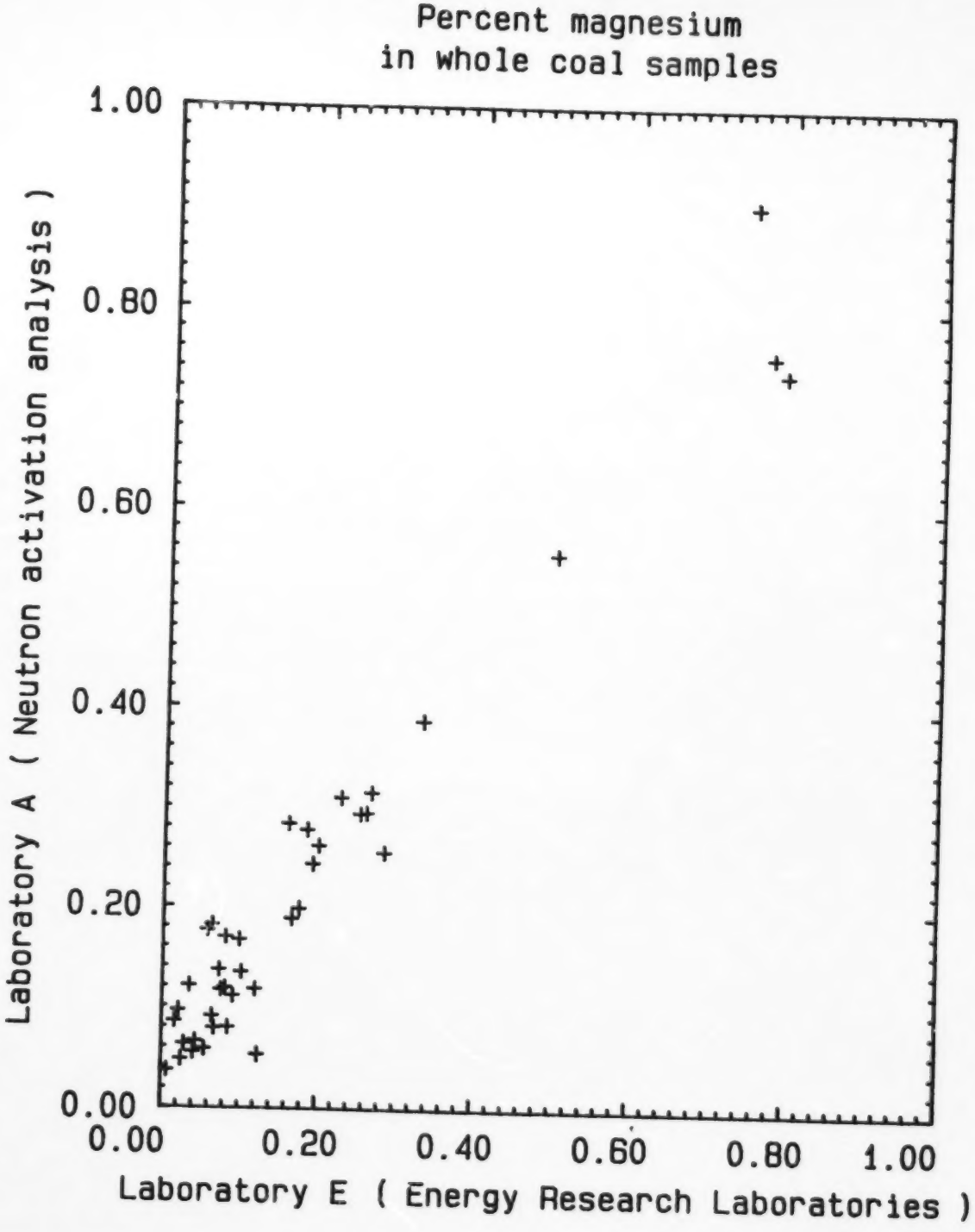

Percent strontium
in whole coal samples
0.080
0.060
0.040
0.020
0.000
Laboratory A (Neutron activation analysis)
0.000
0.020
0.040
0.060
0.080
Laboratory E (Energy Research Laboratories)

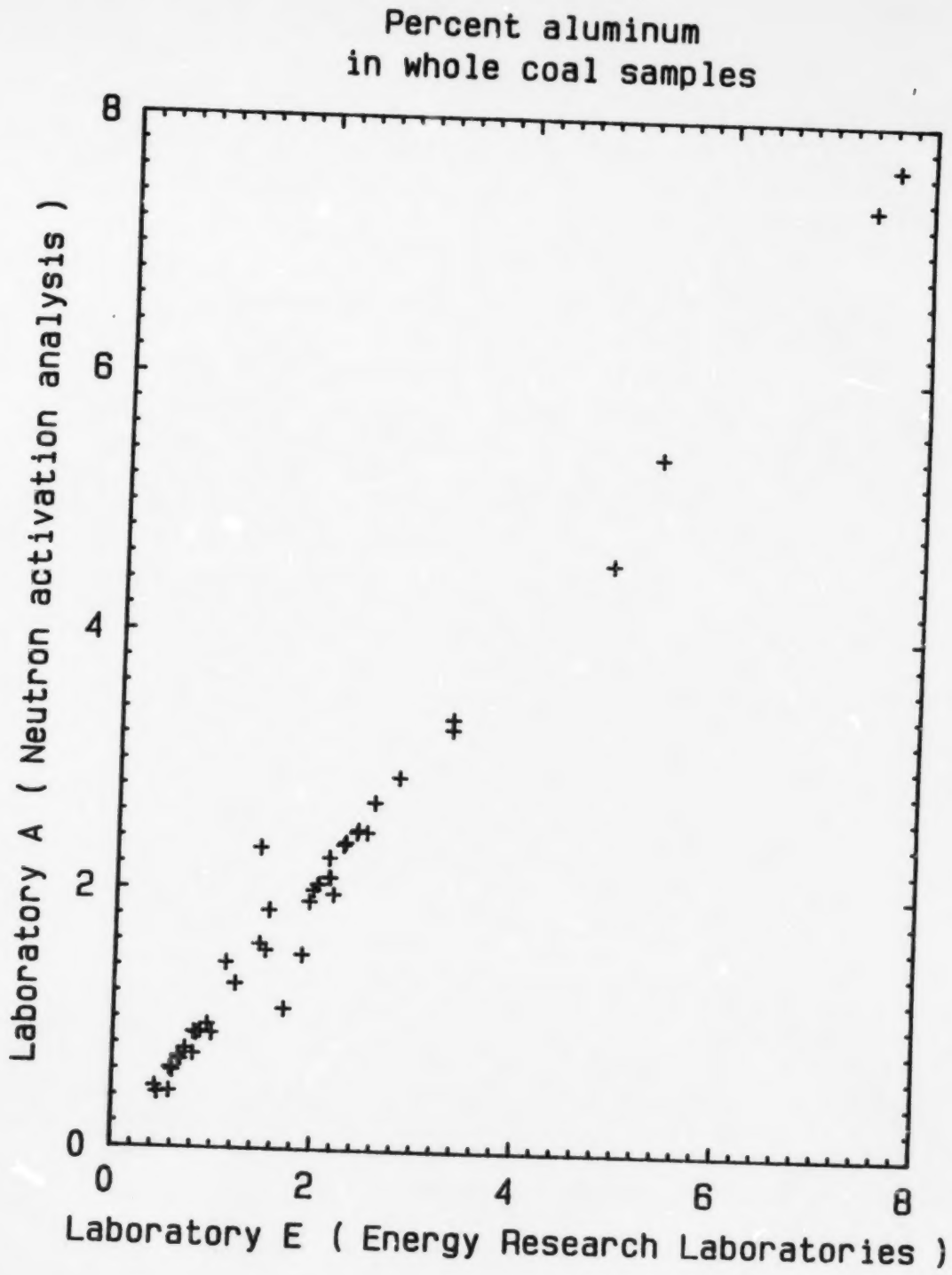

Part per million antimony
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8

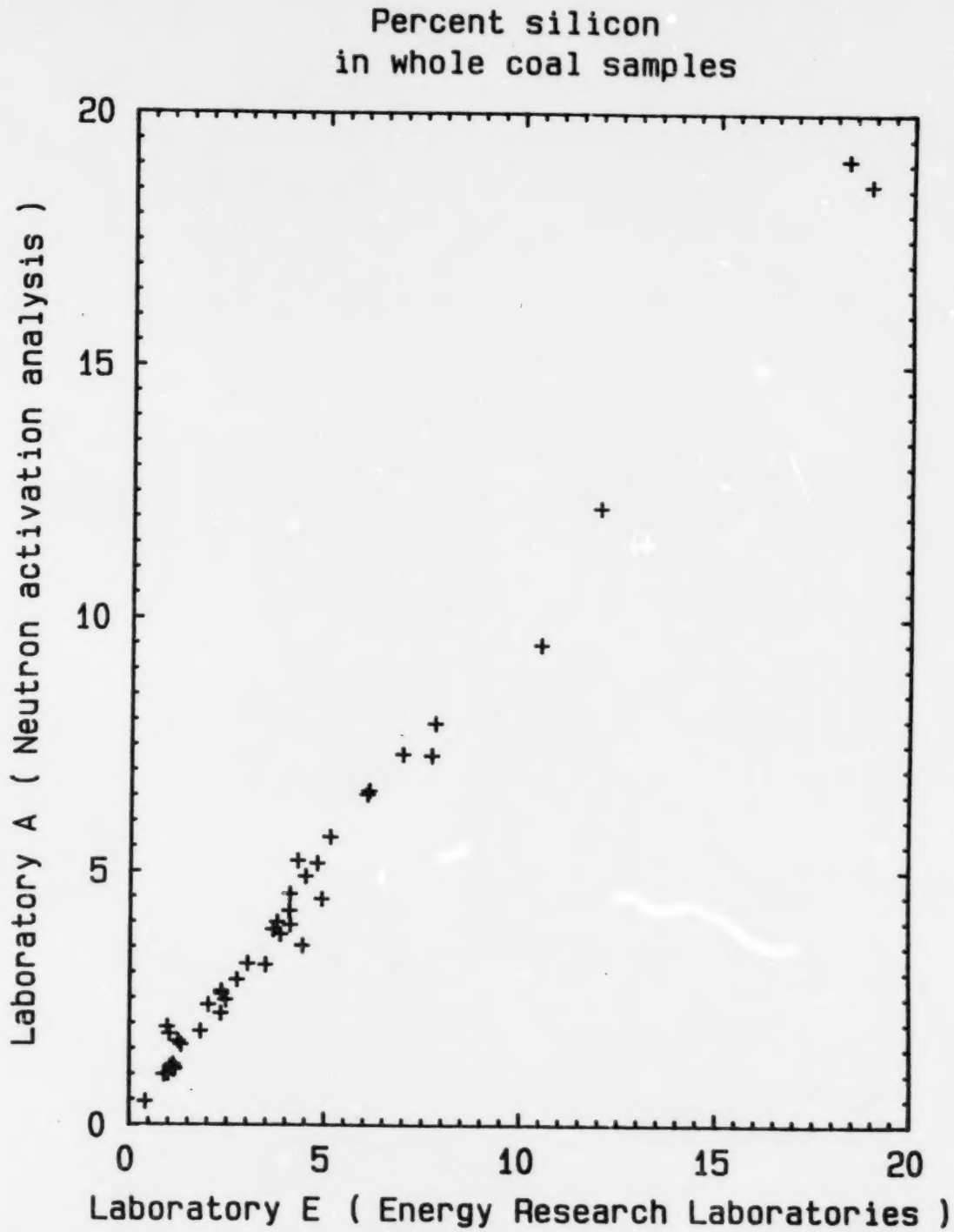

Percent barium
in whole coal samples
0.30
0.20
0.10
0.00
0.00
0.10
0.20
0.30
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

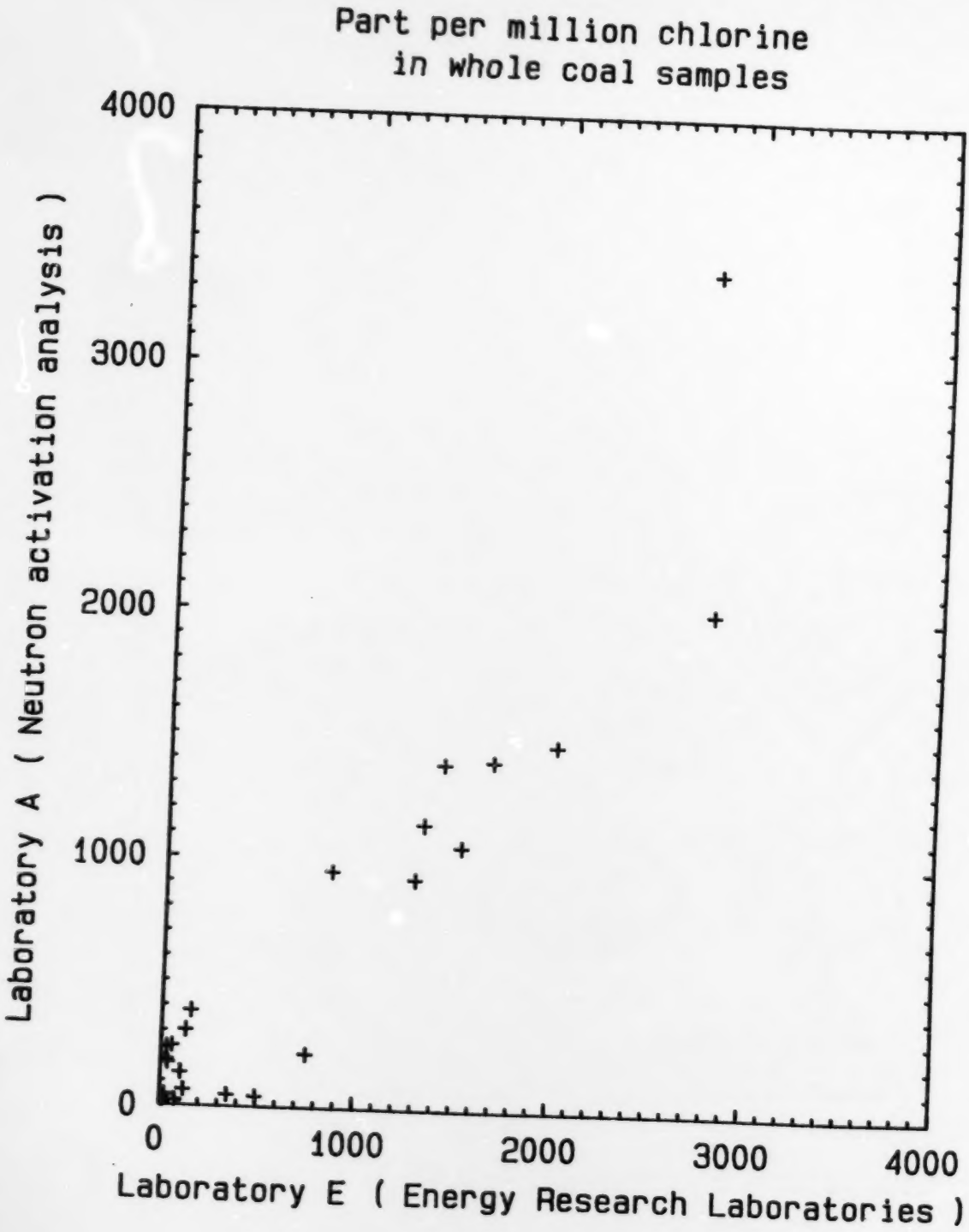

Percent sodium
in whole coal samples
1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
0.80
1.00
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

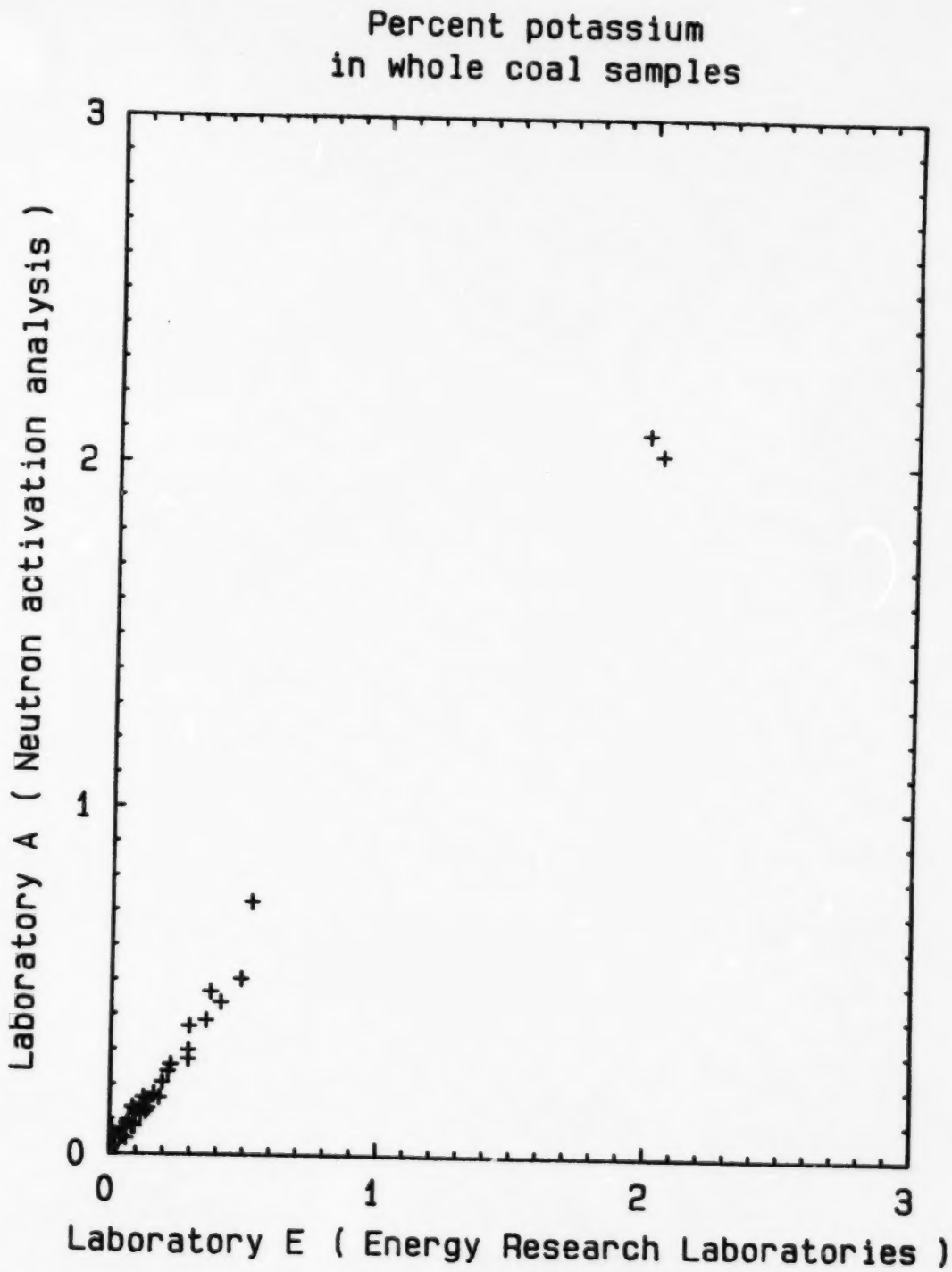

Percent sodium
in whole coal samples
0.200
0.150
0.100
0.050
0.000
0.000
0.050
0.100
0.150
0.200
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

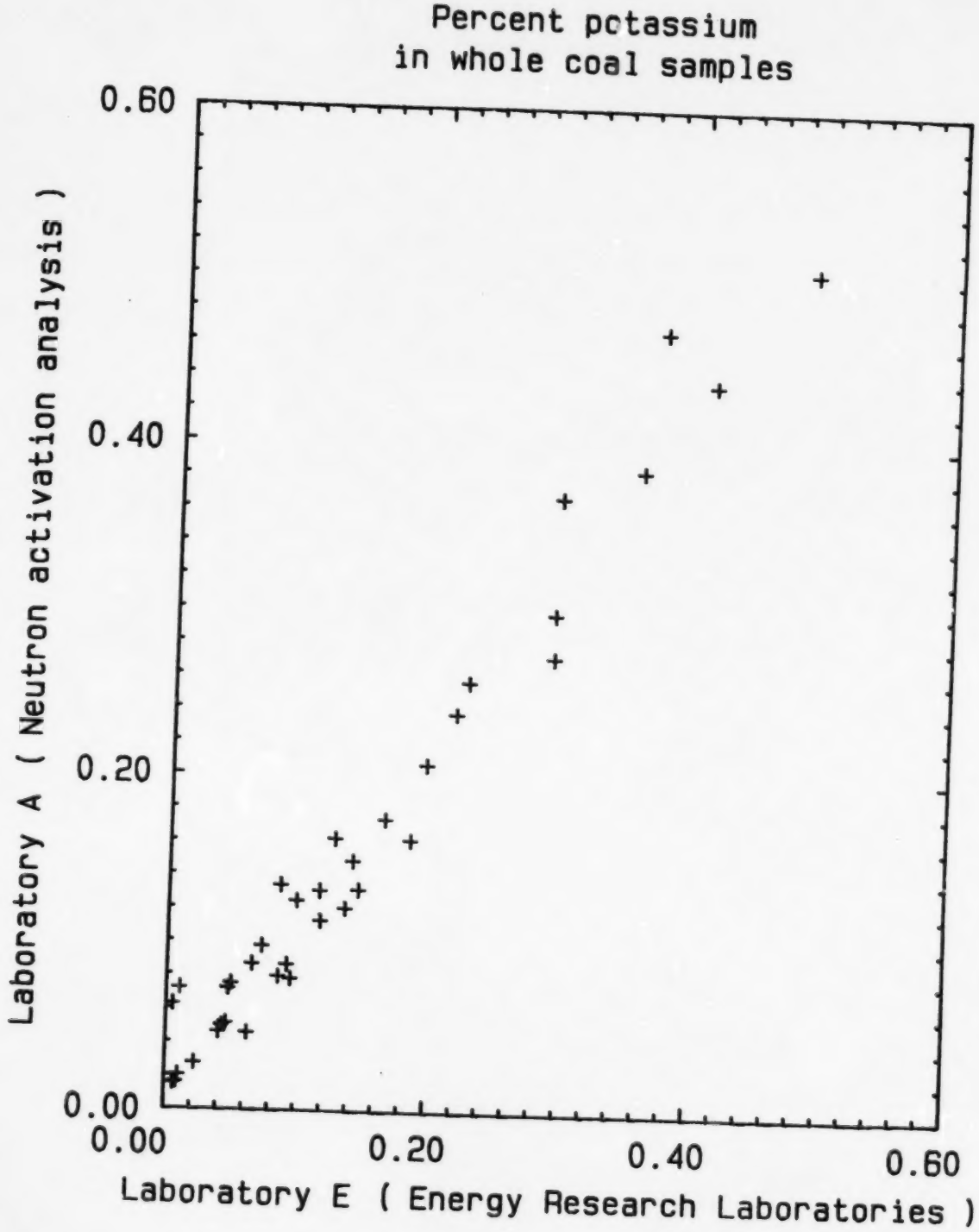

Percent magnesium
in whole coal samples
1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
0.80
1.00
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

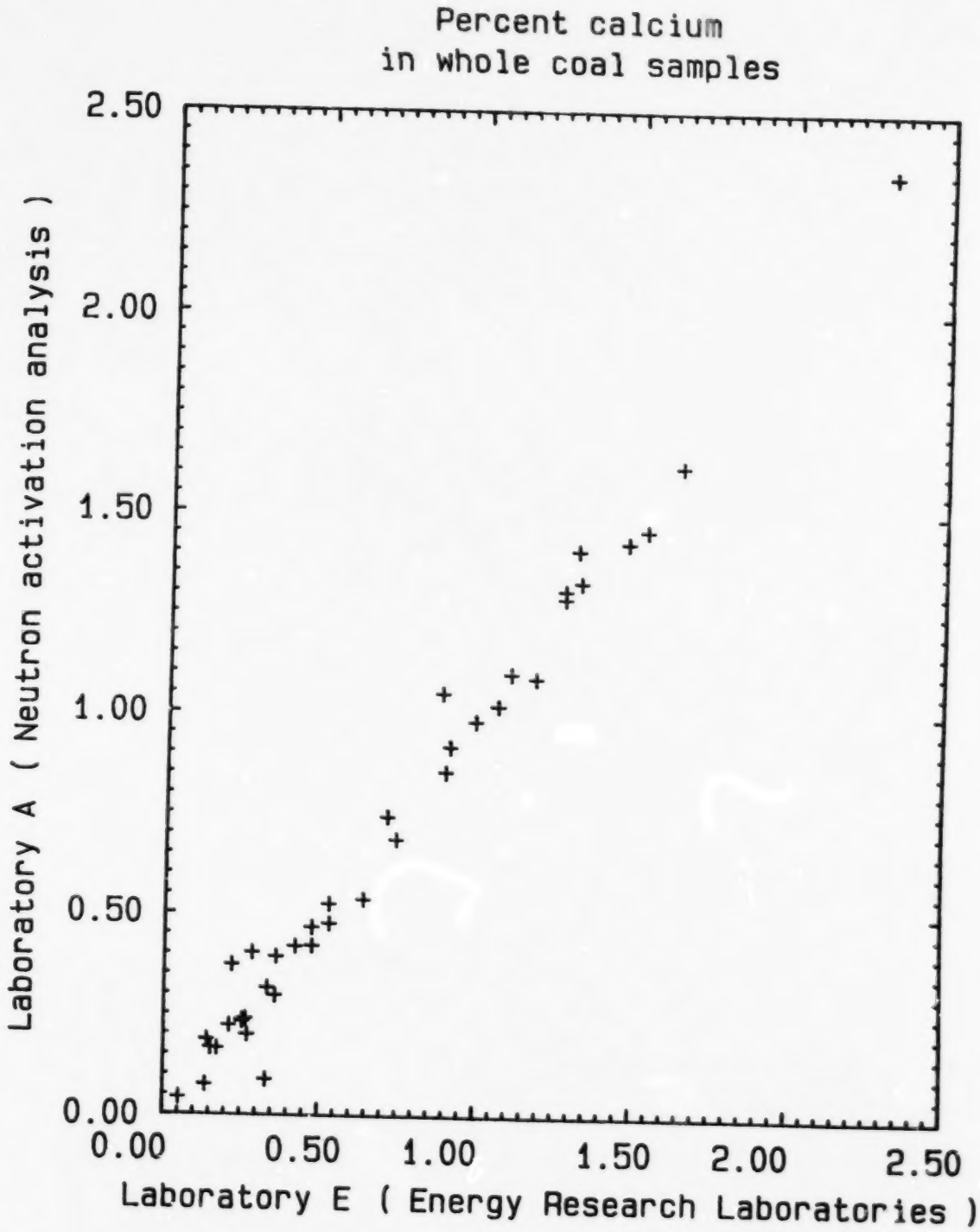

Percent aluminum
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8

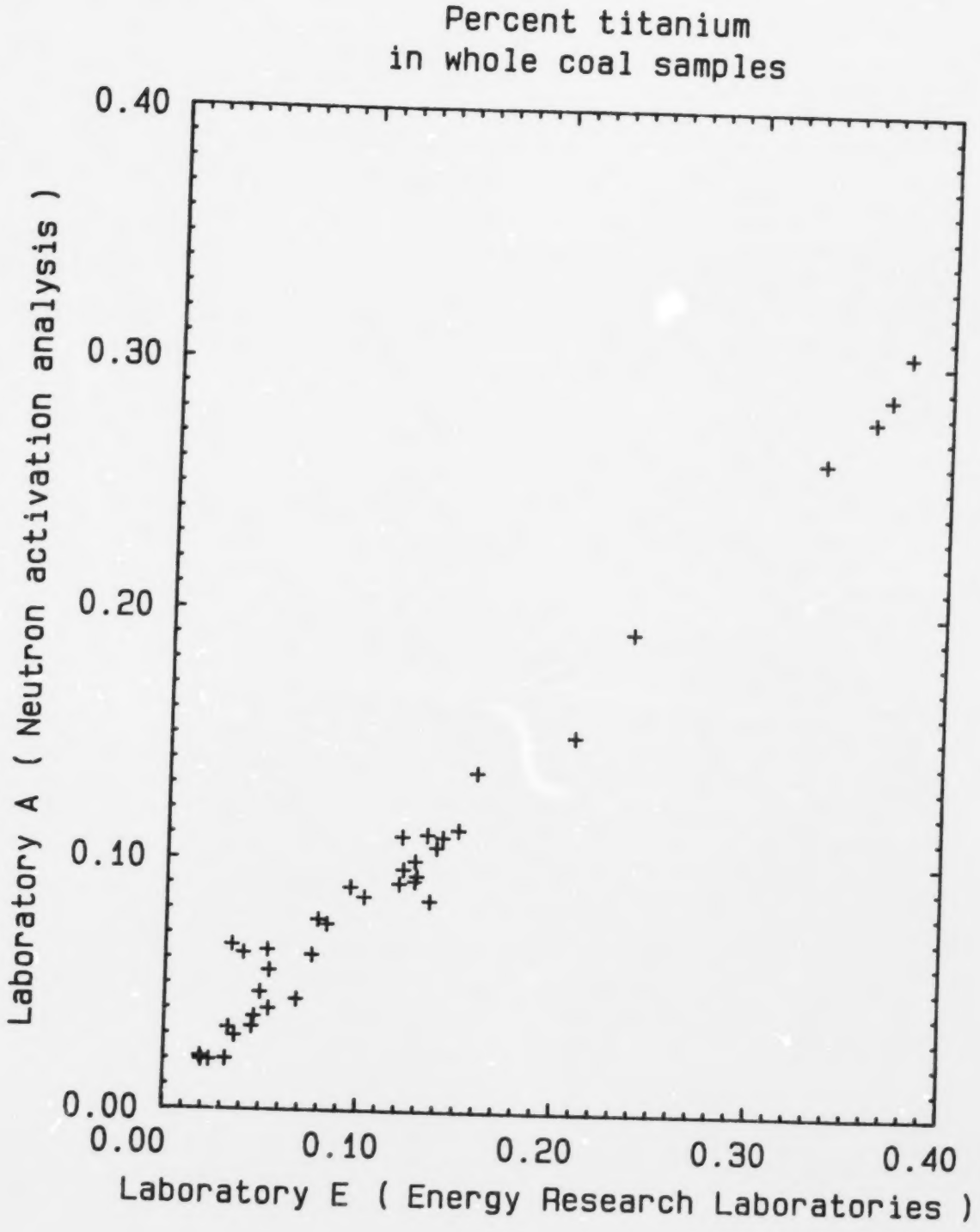

Percent silicon
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
5
10
15
20

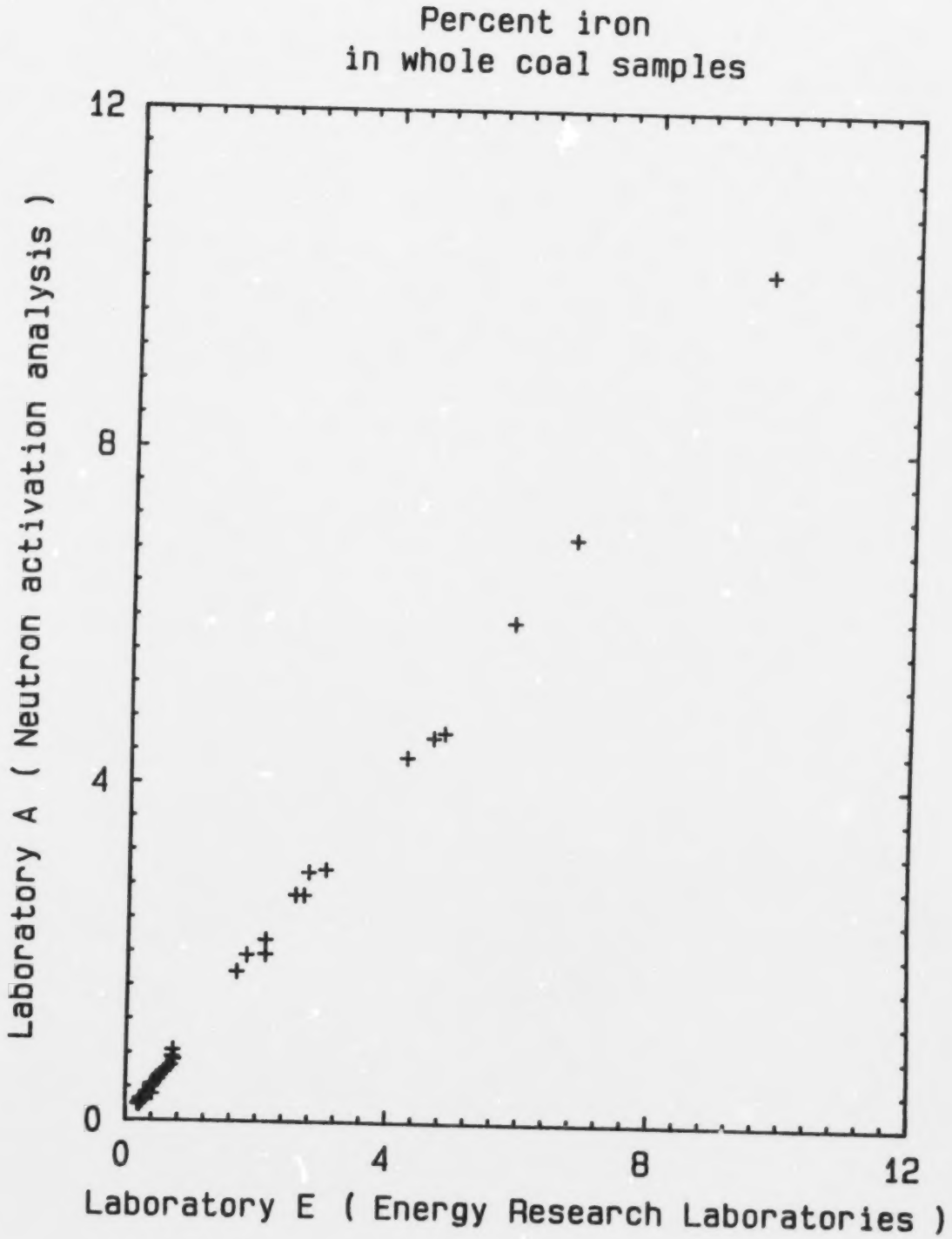

Part per million chlorine
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
1000
2000
3000
4000

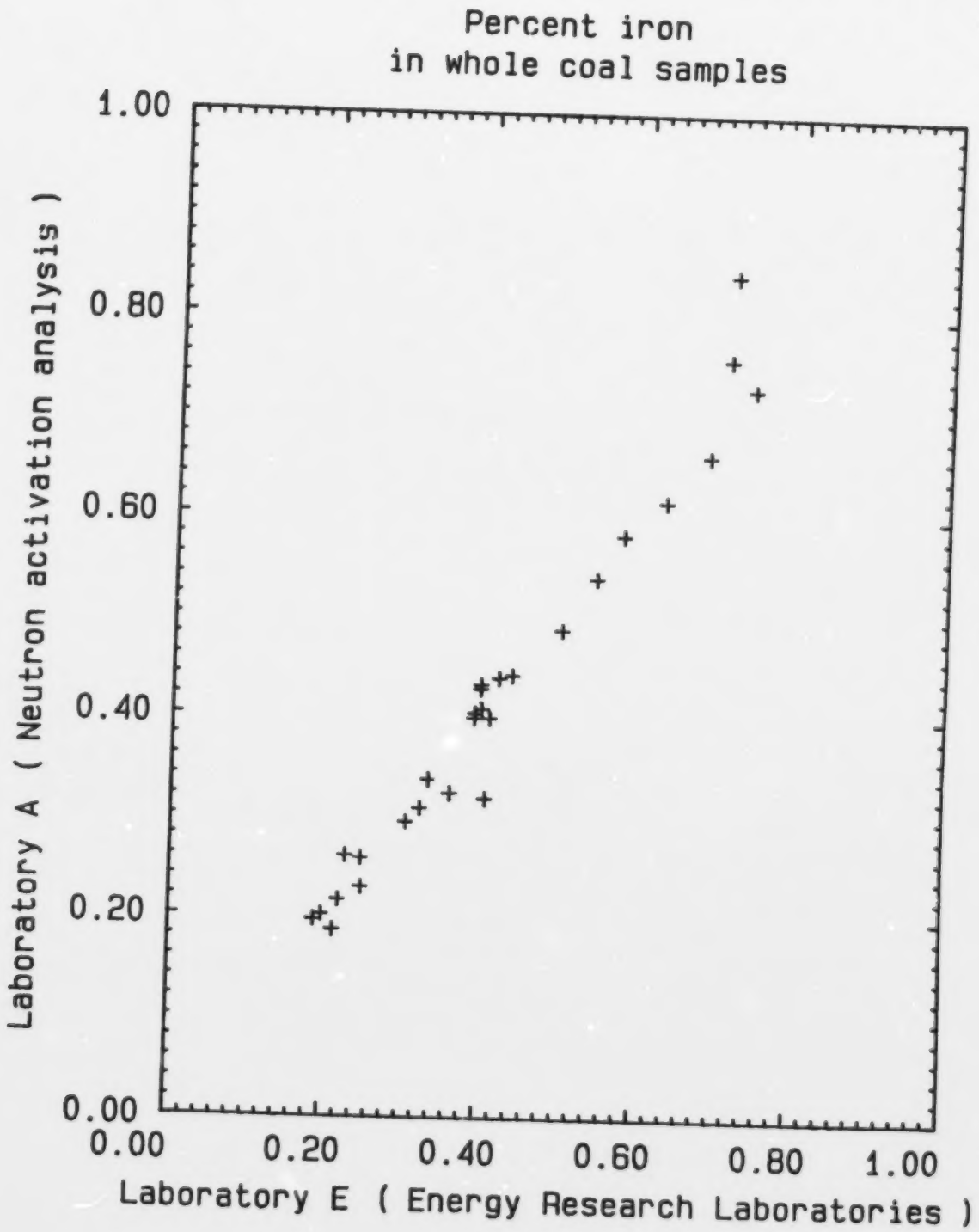

Percent potassium
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
1
2
3
0
1
2
3

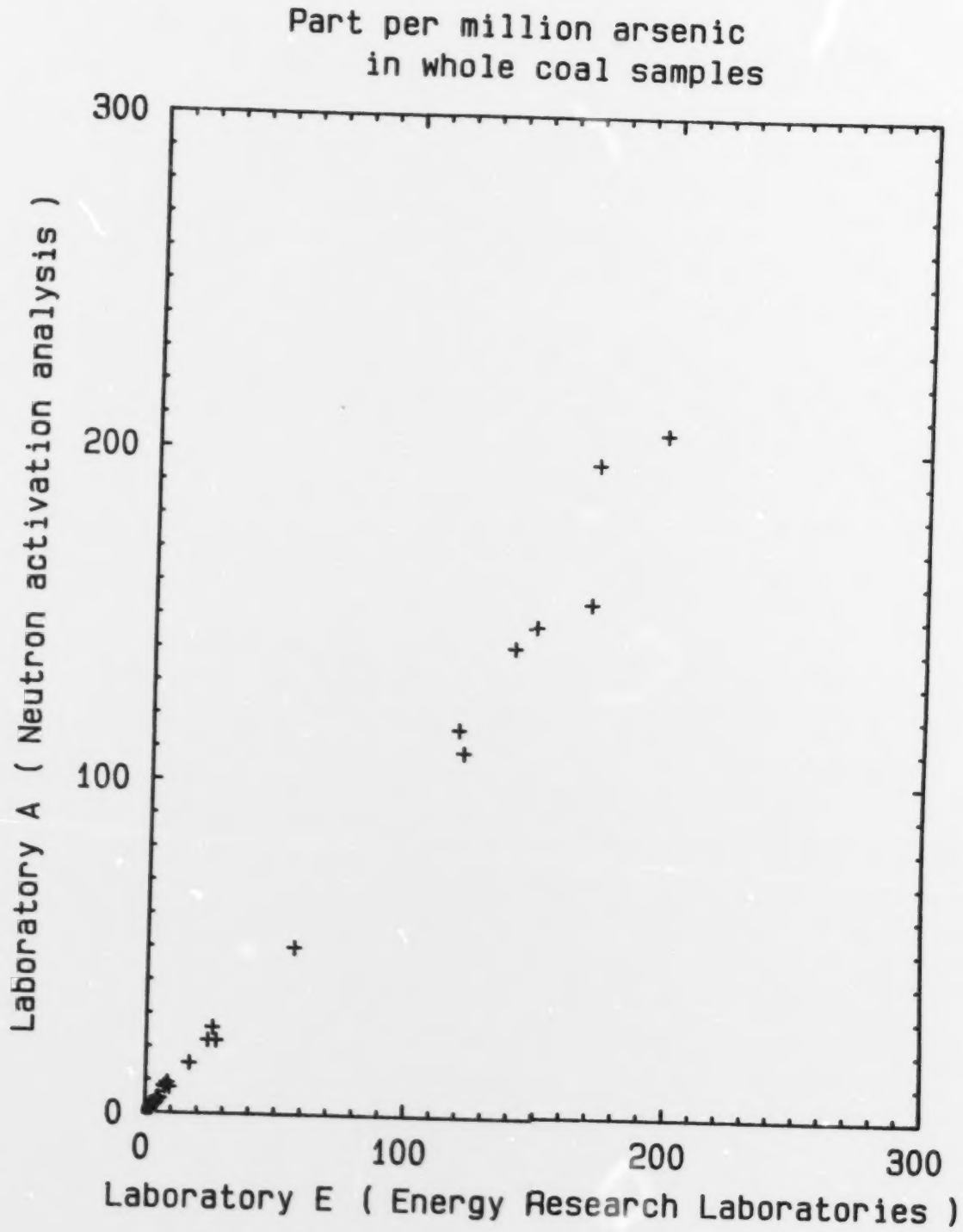

Percent potassium
in whole coal samples
0.60
0.40
0.20
0.00
0.00
0.20
0.40
0.60
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

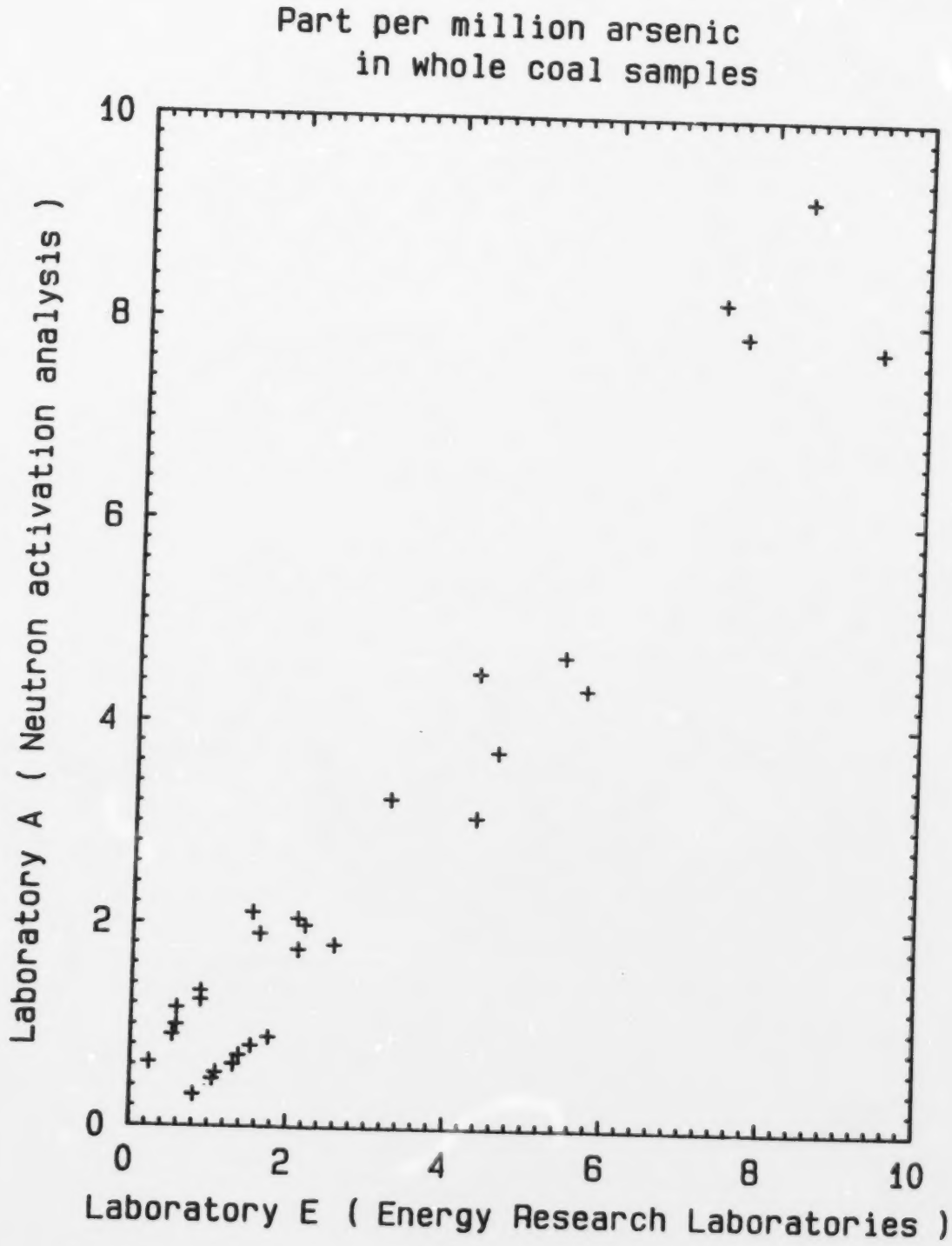

Percent calcium
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0.00
0.50
1.00
1.50
2.00
2.50

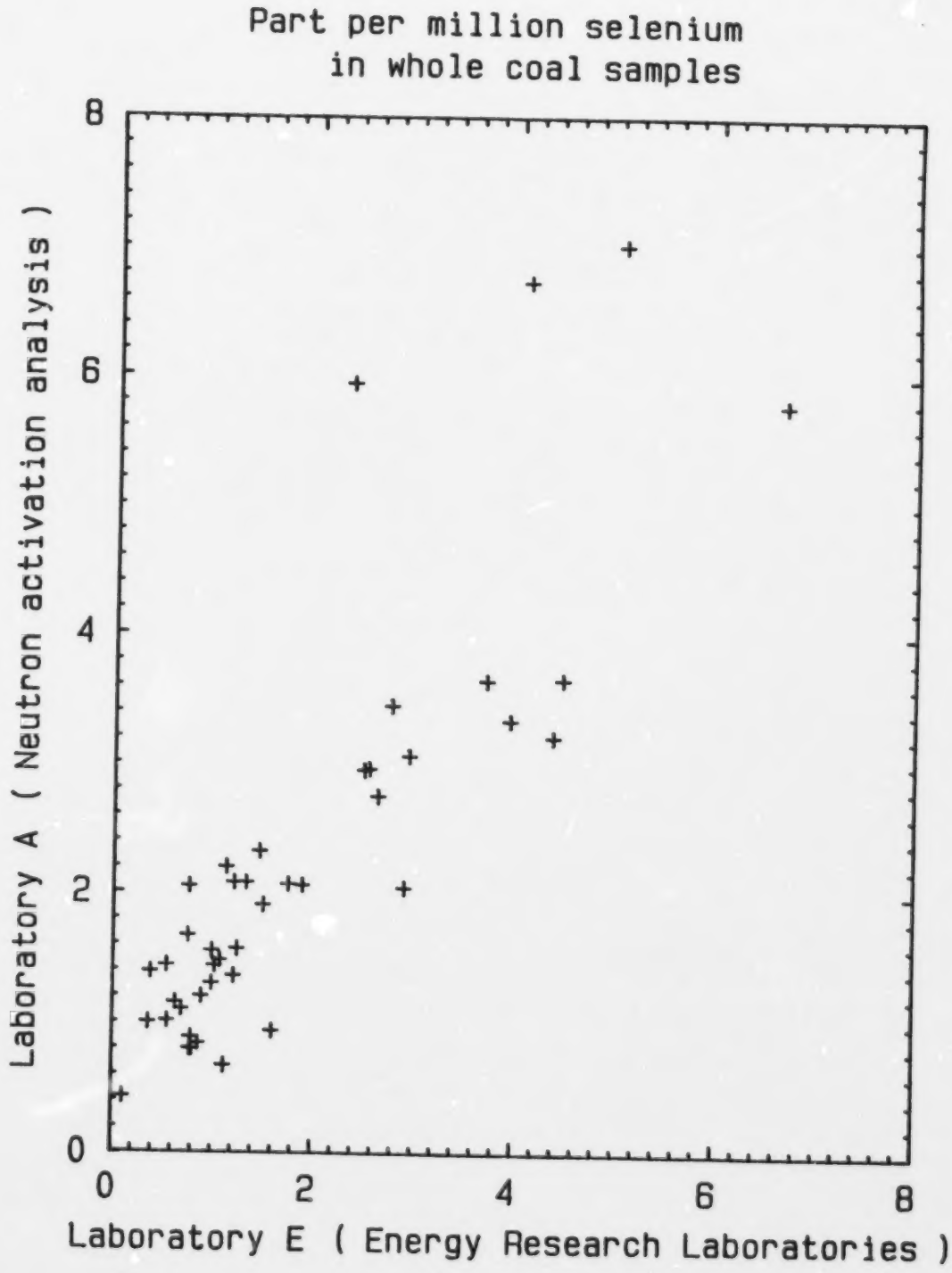

Percent titanium
in whole coal samples
0.40
0.30
0.20
0.10
0.00
0.00
0.10
0.20
0.30
0.40
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

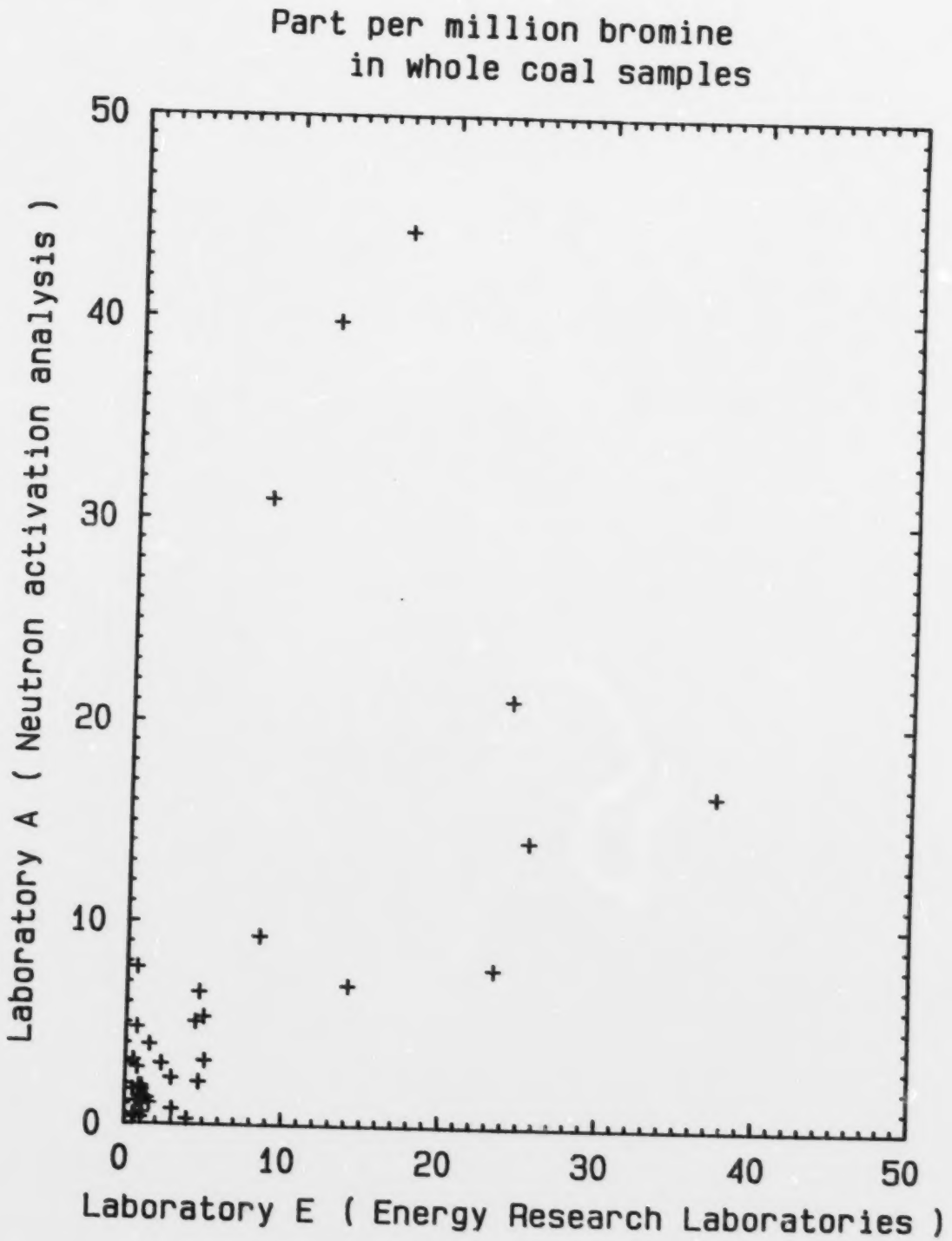

Percent iron
in whole coal samples
12
8
4
0
0
4
8
12
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

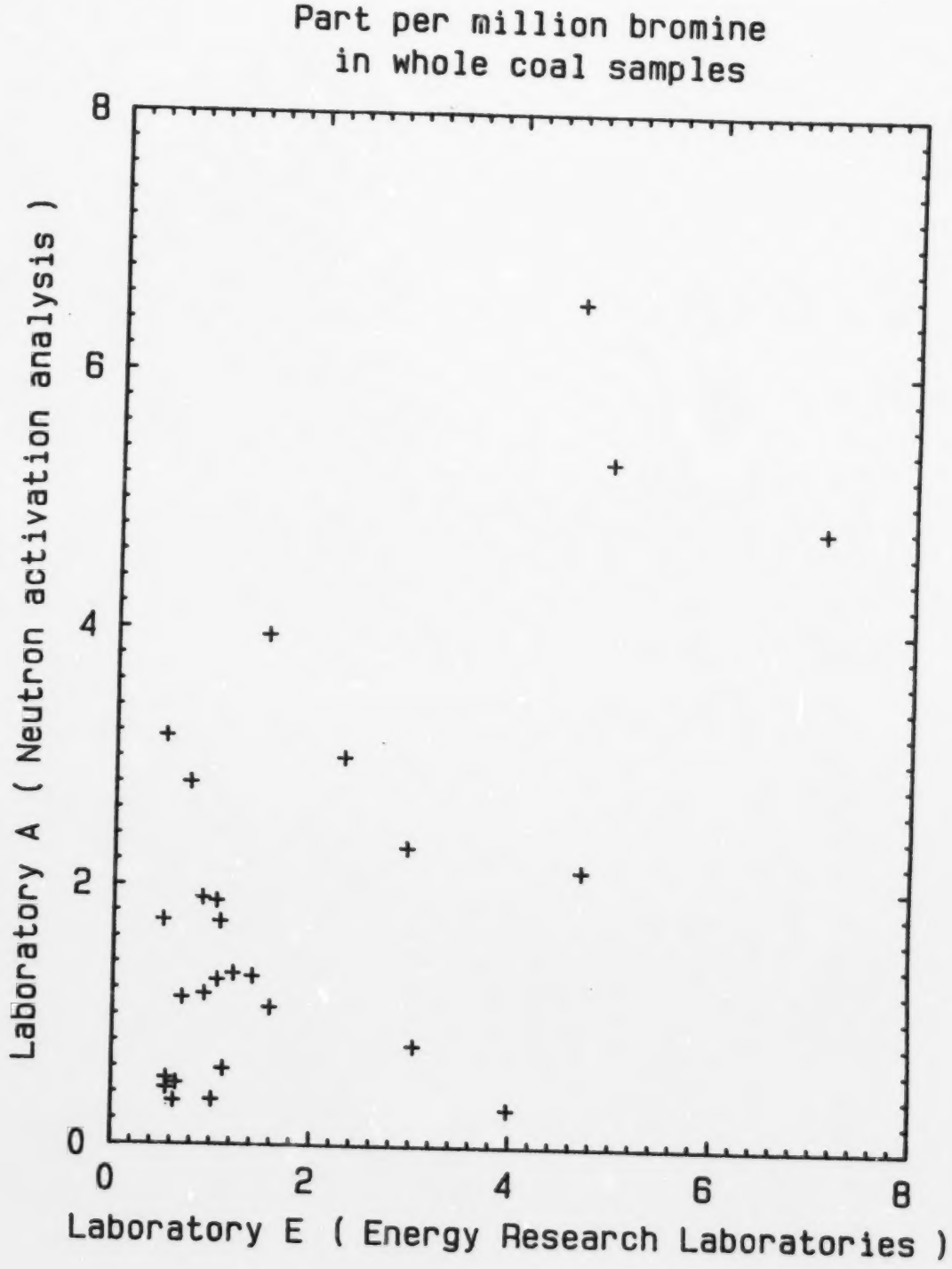

Percent iron
in whole coal samples
1.00
0.80
0.60
0.40
0.20
0.00
Laboratory A (Neutron activation analysis)
0.00
0.20
0.40
0.60
0.80
1.00
Laboratory E (Energy Research Laboratories)

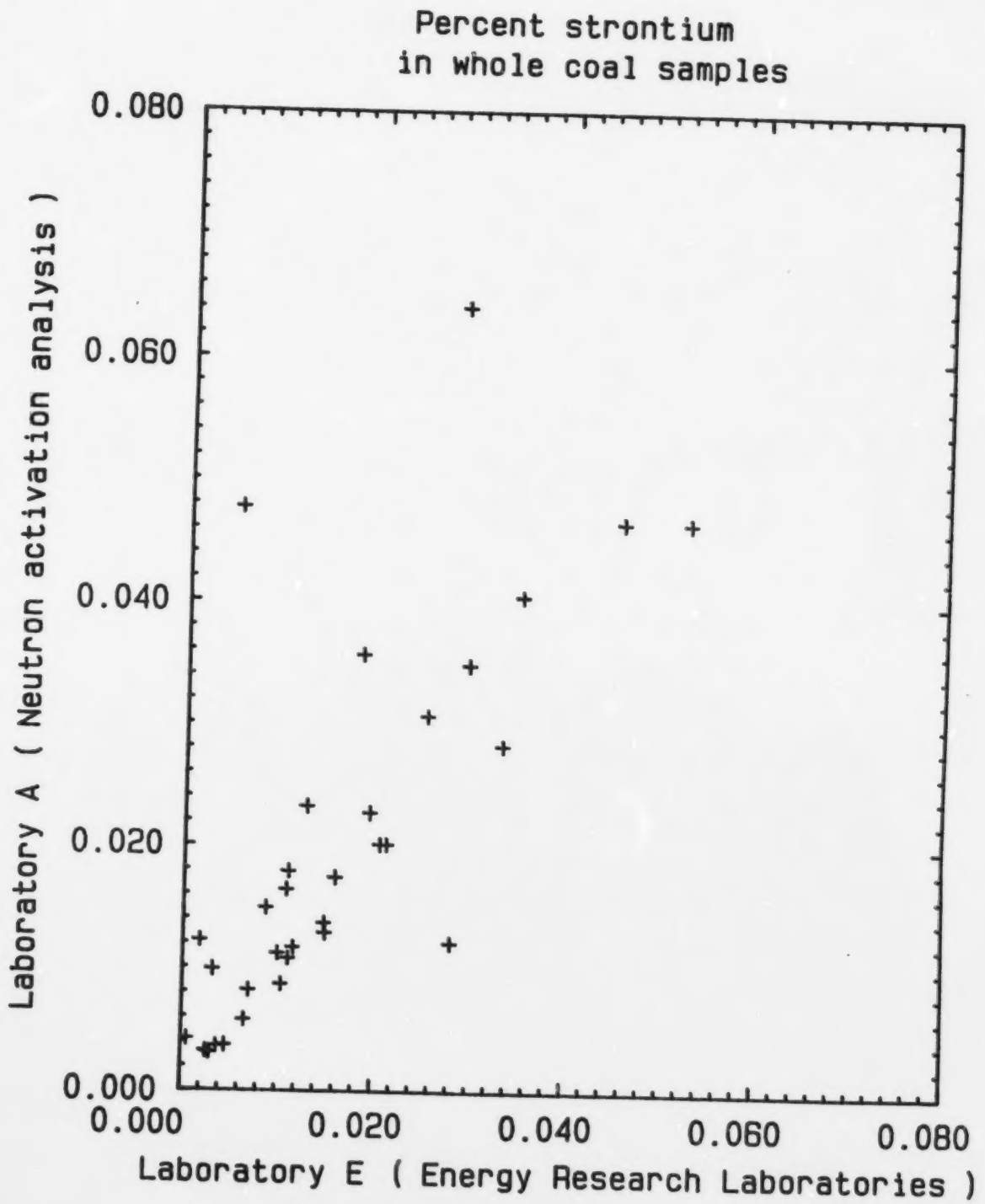

Part per million arsenic
in whole coal samples
300
200
100
0
0
100
200
300
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)

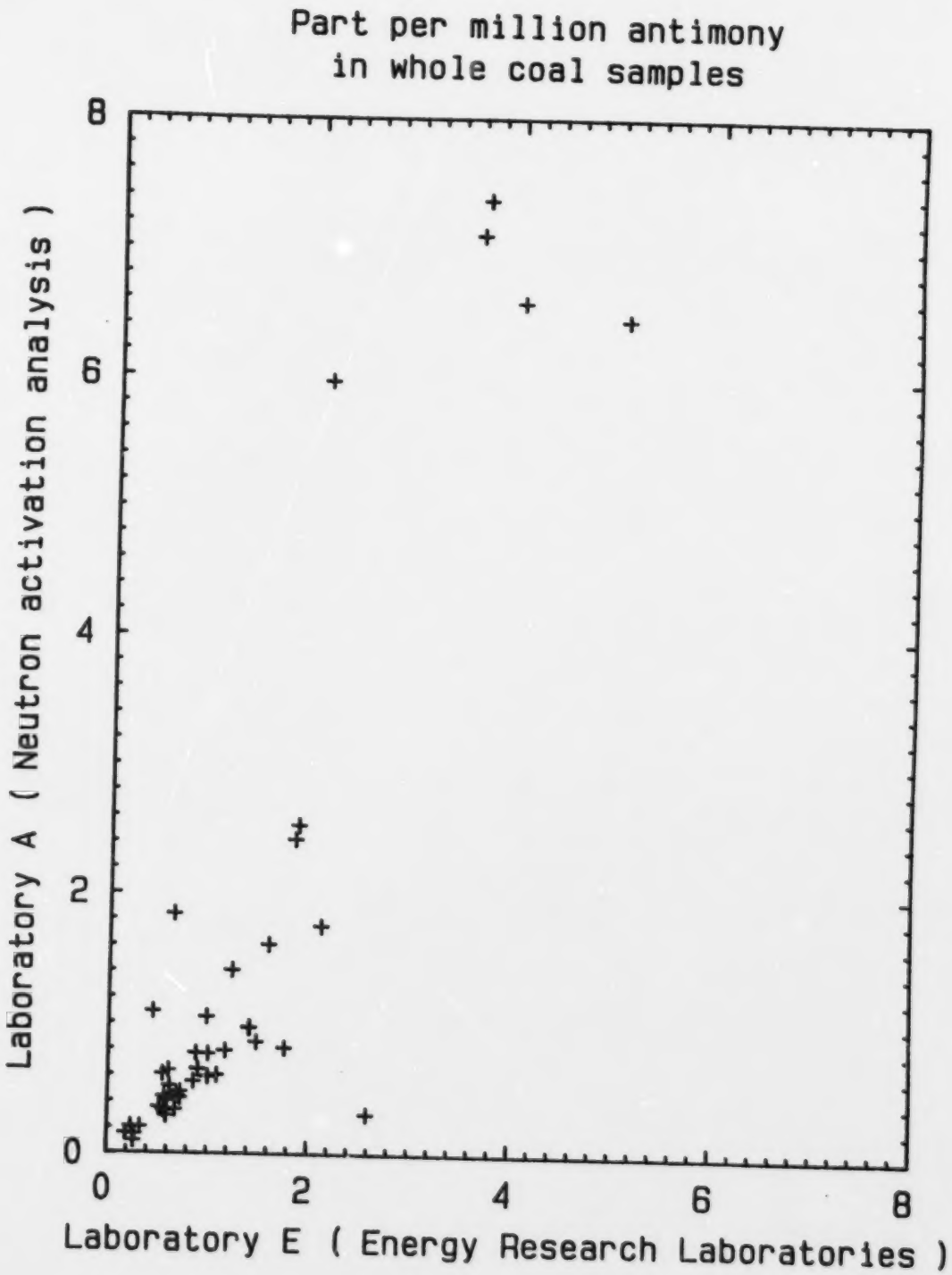

Part per million arsenic
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8
10

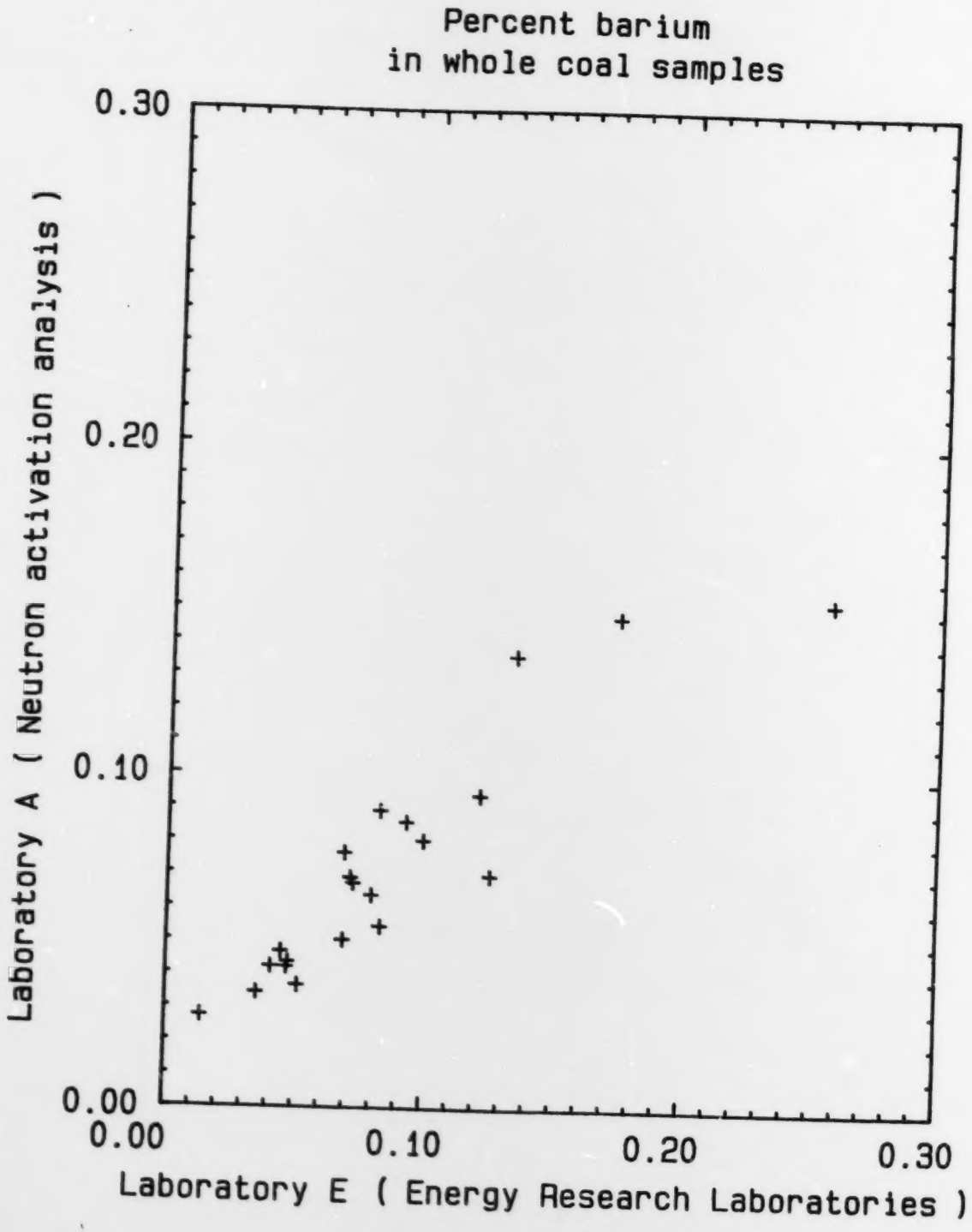

Part per million selenium
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8


Part per million bromine
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
10
20
30
40
50


Part per million bromine
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8


Percent strontium
in whole coal samples
0.080
0.060
0.040
0.020
0.000
Laboratory A (Neutron activation analysis)
0.000
0.020
0.040
0.060
0.080
Laboratory E (Energy Research Laboratories)


Part per million antimony
in whole coal samples
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)
0
2
4
6
8


Percent barium
in whole coal samples
0.30
0.20
0.10
0.00
0.00
0.10
0.20
0.30
Laboratory A (Neutron activation analysis)
Laboratory E (Energy Research Laboratories)